

## UNITED STATES AIR FORCE RESEARCH LABORATORY



### VACUUM DEPOSITED ORGANIC LIGHT EMITTING DEVICES ON FLEXIBLE SUBSTRATES

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**FOR THE COMMANDER**



MARIS M. VIKMANIS  
Chief, Crew System Interface Division  
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## 13. ABSTRACT (Maximum 200 words)

The objective of this eight year program was to demonstrate both passive and active matrix, flexible, small scale displays based on small molecular weight organic light emitting device (OLED) technology. The team comprised the University of Southern California, Universal Display Corporation, and Hughes Research Laboratories, and was led by Princeton University (PI: Stephen R. Forrest). The primary platform (device structure for research) at the outset of the program in 1994 was a stacked, full color OLED (SOLED) based on fluorescent emission. It was our objective to integrate SOLEDs on flexible active matrix backplanes based on small arrays of silicon-on-insulator transferred in thin film form from a silicon wafer "handle." Among the accomplishments of this program were the demonstration of transparent (TOLED), stacked flexible (FOLED), and ultrahigh efficiency phosphorescent OLEDs (PHOLED). Also, the use of several manufacturing technologies for the production of OLED displays were created and demonstrated, most notably the proprietary process of organic vapor phase deposition (OVPD).

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## FOREWORD

This Grant F33615-94-1-1414 (ASTARS<sup>1</sup> WU<sup>2</sup> A9400101 was selected under Defense Advanced Research Projects Agency (DARPA) Broad Agency Announcements (BAA) 93-19 and BAA 97-31, both entitled "High Definition Systems (HDS)." The title of the original proposal was "Novel, Full Color Flat Panel Display Technology Employing High Performance Crystalline Organic Semi Conductor Light Emitting Diodes" This grant from the government to the Princeton University required the government to provide 100% of the total project funding of \$5,438,957 under DARPA Order A940 to Dr. Hopper at the Air Force Research Laboratory (AFRL) as DARPA Agent. Mr. Gurdial Saini of AFRL served as the contract monitor. Performance was over the period 13 June 1994 through 30 April 2002. The original grant based on the 1993 proposal was for the period 13 June 1994-31 December 1997 in the amount of \$1,541,000. A subsequent proposal against the 1997 BAA resulted in an expansion of this grant by an additional \$3,094,957 for work accomplished from September 1997 to 30 April 2002. In addition, a \$260,000 organic laser task (October 1998-March 2000) and a \$530,000 blue phosphor task (January 2001-January 2002) were added in 1997 and 2001, respectively.

In addition to this report, the results of this eight-year project are documented in 62 patents listed in Appendix A and in 87 publications listed in Appendix B). Personnel involved and graduate degrees awarded with funding under this effort are listed in Appendices C and D. An extensive pictorial presentation of the results are available in the form of the 3 May 2002 final review presentation charts in Appendix E.

Additional detail on accomplishments under this grant during the period June 1994 to June 1997 has been published in an earlier technical report:

Stephen R. Forrest, Mark E. Thompson, and Juan Lam,  
"Novel, Full Color Flat Panel Display Technology Employing High Performance  
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AFRL-HE-WP-TR-1998-0098, 44 pages (May 1998).  
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The technical review of this document was accomplished by Dr. Hopper and Mr. Saini of AFRL.

This technical report is available electronically in color from the author at Princeton University.

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<sup>1</sup> A Science and Technology Activity Reporting System (ASTARS)

<sup>2</sup> Workunit (WU)

## **PREFACE**

The objective of this applied research program was to create a small molecule organic light emitting diode (OLED) display device technology starting from basic research results on materials that has been funded in the early 1990s by the Air Force Office of Scientific Research and the Office of Naval Research.

Princeton University in Princeton NJ assembled a team comprising the University of Southern California (USC) in Los Angeles CA, Hughes Research Laboratories (HRL) in Malibu CA, and the Universal Display Corporation (UDC) in Ewing NJ. Princeton University concentrated on the development of flexible, transparent, stacked, and ultrahigh efficiency OLEDs, packaged passive matrix (PM) display pixel arrays, accomplished initial reliability testing, experimented with organic laser contacts, demonstrated organic transistors, and demonstrated roll-to-roll processing. USC developed organic materials for high reliability, efficient, saturated color OLEDs. HRL developed a silicon thin film transistor (TFT) active matrix (AM) on glass and flexible substrates using a lift-off technique, and accomplished qualification of the technology potential for DOD and civilian applications. UDC accomplished reliability studies of active matrix and passive matrix (AM & PM) flexible displays, developed display manufacturing processes, built a scale-up facility to build manufacturing prototypes, and formed strategic alliances necessary to transition the technology to high volume markets.

The research reported here has been transitioned to industry, to the DARPA Flexible Display Program (two on-going efforts awarded in 2000 and completing in 2003) and to a new Army Research Laboratory (ARL) Electronic Display Program (two efforts awarded in August 2002).

## **ACKNOWLEDGEMENTS**

We gratefully acknowledge the financial support received from DARPA under Grant Number F33615-94-1-1414. We thank Dr. Darrel G. Hopper, and Mr. Gurdial S. Saini of AFRL for their support throughout the project.

## 1. SUMMARY

The objective of this eight-year program was to demonstrate both passive and active matrix, flexible, small-scale displays based on small molecular weight organic light emitting device (OLED) technology. The team included the University of Southern California, Universal Display Corporation, and HRL Laboratories, and was led by Princeton University (PI: Stephen R. Forrest). The primary platform at the outset of the program in 1994 was a stacked, full color OLED, or SOLED, based on fluorescent emission. The approach was to integrate SOLEDs on flexible active matrix backplanes based on small arrays of silicon on insulator transferred in thin film form from a Si wafer "handle". As the program progressed several major developments caused a change of course from these initial directions to explore far more fertile areas of advance. Some 14 major achievements of accomplished during this project are listed below.

- Demonstration of a transparent top contact OLED
- Demonstration of a stacked, full color OLED
- Demonstration of a flexible small molecular weight OLED, leading to demonstration of the first, full-motion video, flexible passive matrix display
- Demonstration of highly efficient process of electrophosphorescence (nearly 100% internal quantum efficiency) leading to the demonstration of very high efficiency OLED displays
- Adaptation of organic vapor phase deposition manufacturing process to fabrication of displays
- Demonstration of very long lifetime red and green emitting phosphorescent OLEDs
- Demonstration of several high efficiency light out-coupling schemes from OLEDs
- Understanding physical processes leading to charge transport in thin film organic devices
- Understanding of the luminescent properties of fluorescent and phosphorescent OLEDs
- Demonstration of rapid, non-destructive display patterning via cold welding followed by lift off
- Demonstration of high mobility organic thin film transistors based on the organic vapor phase deposition of pentacene channels
- Establishment of a display pilot line by a team member (Universal Display Corporation)
- Demonstration of the process of phosphor sensitized fluorescence, leading to very high efficiency fluorescent OLEDs
- Demonstration of an OLED integrated with a flexible Si AM display backplane

## 2. INTRODUCTION

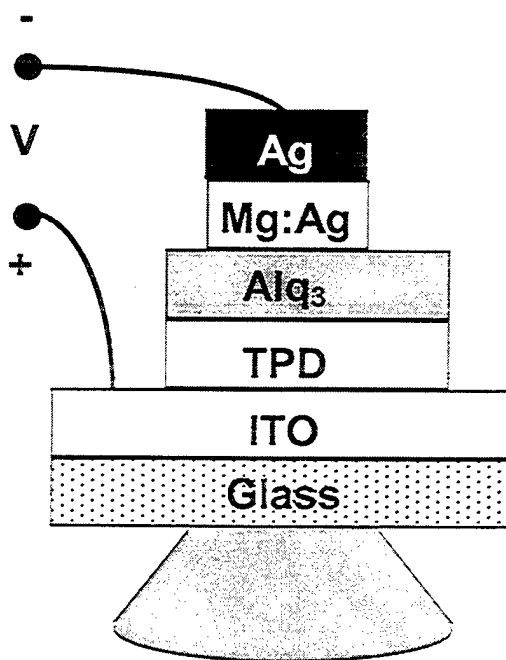
A conventional OLED structure based on small molecular weight compounds is shown schematically in Figure 1. Briefly, the device is structured as follows: On top of a glass substrate, typically equal to or less than 1 mm in thickness, is grown a transparent conducting anode using such materials as indium tin oxide (ITO). This anode is often deposited by sputtering in vacuum prior to the deposition of the organic layers. Next, a material that preferentially conducts holes, or the hole transporting layer (HTL) is deposited by vacuum thermal evaporation in a chamber whose background pressure is  $<10^{-6}$  Torr to a thickness of approximately 50 nm. Next follows the deposition of an equal thickness of an electron transporting layer (ETL). In the original OLEDs demonstrated in 1985, the ETL material also emitted green light, making the ETL serve the dual purpose of transporting electrons as well as providing the light emission. The device is then completed by deposition of a low work function metal cathode providing efficient electron injection into the ETL. Metal such as mixtures of Mg and Ag, or LiF and Al are most frequently used for this purpose.

In operation, the cathode is connected to the negative terminal of a power supply, and the anode is grounded. Then, electrons and holes are injected from the cathode and anode contacts, respectively, and are transported by the ETL and HTL to the interface between these two layers. At this point, the electron and hole form a coulombically bound state on a molecule in the ETL. This state, which can also be considered a molecular excited state, called an exciton, can diffuse through the ETL until the electron and hole recombine. The energy lost in that recombination process generates either heat (if the recombination is via a defect), or light. The light is then emitted and those photons which emerge within the critical angle of the glass/air interface are then emitted and are seen by the observer. An OLED such as that in Figure 1 typically has an external quantum efficiency (i.e. the ratio of electrons injected to the number of photons observed) of ~1%, and an operational lifetime of ~1000 hrs.

The device can be made much more efficient by "doping" either the HTL or ETL with a highly luminescent molecule, whose energy of luminescence is lower than that of the host HTL or ETL material (i.e. it is red shifted in color). Then, as excitons are formed in the host at the HTL/ETL interface, it becomes energetically favorable for the excited state to transfer from the host to the luminescent molecule. Because the luminescent molecule (also known as the lumophore) is only at low concentrations (1%-10%) within the host, they are isolated from each other. Hence, the exciton cannot easily diffuse around the material layer where it might encounter a non-radiative defect site. In this case, the quantum efficiency of the device can be greatly improved. Indeed, using phosphor dopants developed in this program, along with "blocking layers" that energetically trap the exciton within the luminescent zone of the OLED, we have observed ~20% external quantum efficiency, corresponding to ~100% internal efficiency for phosphorescent OLEDs. Here, blocking layers are such that they have energy gaps larger than that of the luminescent layer such that molecular excited states need to gain energy to hop to molecules within the blocking layer. The blocking layer thickness is generally kept thin (~10 nm or less) to avoid increasing the operating voltage of the OLED.

Indeed, by keeping the entire thickness of the resistive organic layers to  $\sim 100$  nm, the operating voltage is typically  $\sim 6$  V.

Finally, the doping of the emission zone also increases the operational lifetime of the OLED. Doped OLEDs, of the type investigated in this program, have operating lifetimes approaching 1,000,000 hrs. in some cases. Typical operating lifetimes are  $\sim 50,000$  hrs for the doped red and green OLEDs developed in this program (conditions: room temperature and display luminance of about  $100 \text{ cd/m}^2$ ). Here, lifetime is defined as the time for the luminance to decrease to half of its initial value.



**Figure 1:** Schematic diagram of a simple organic light emitting device. Here, Alq<sub>3</sub> is an electron transporting and green emissive material, and N,N-di-(3-methylphenyl)-N,N diphenyl-4,4-diaminobiphenyl (TPD) is a hole transport material.

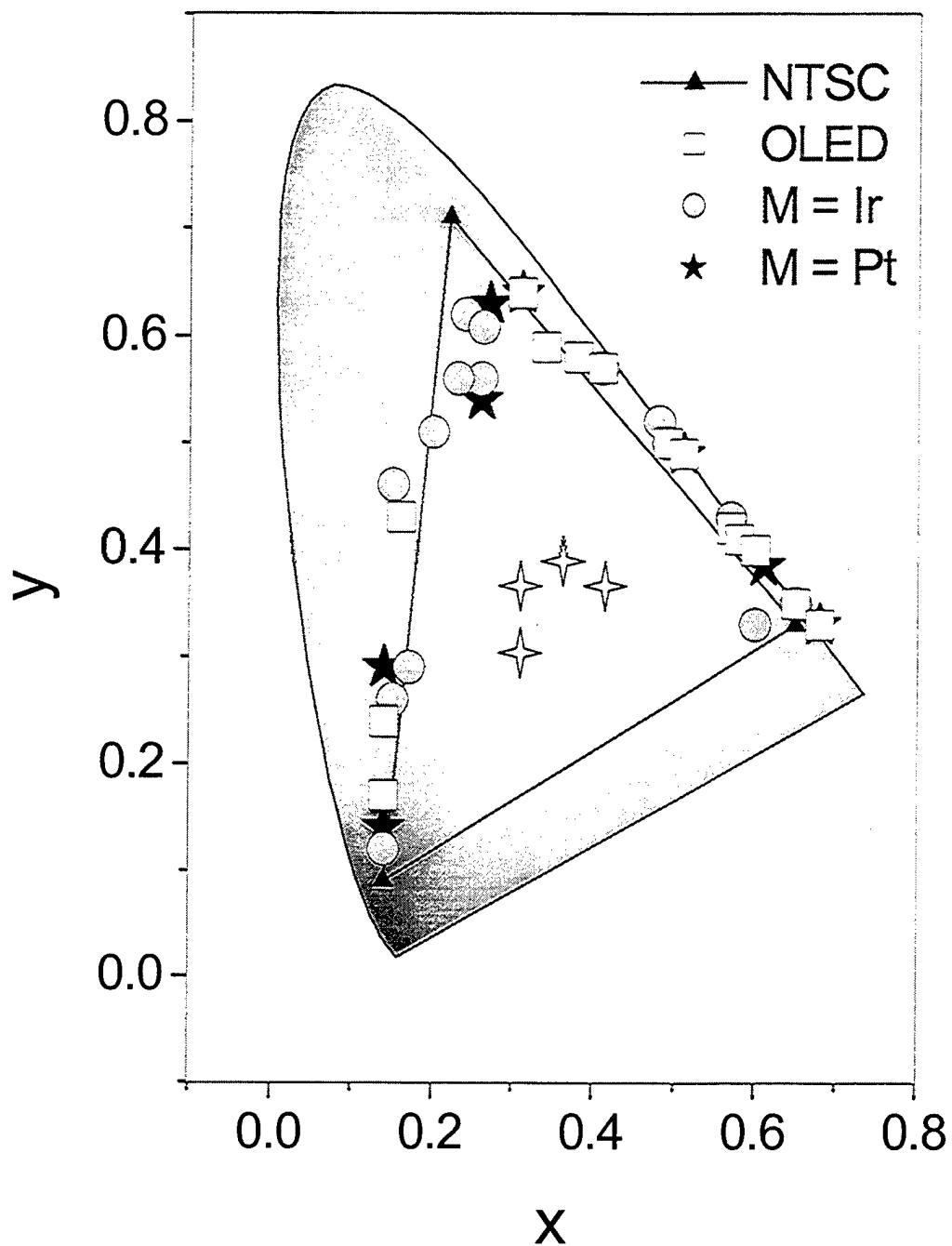
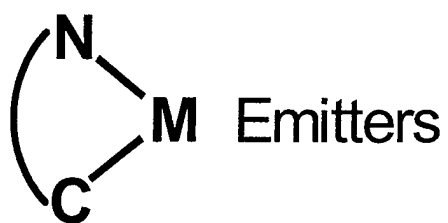
### 3. METHODOLOGY AND RESULTS

We now discuss in detail some of the highlights of the accomplishments of our team. In Appendix E we provide briefing materials from the May 3, 2002 final review. Additional detail on accomplishments under this grant during the period 13 June 1994 to 12 June 1997 has been published in an earlier technical report by Stephen R. Forrest, Mark E. Thompson, and Juan Lam, entitled "Novel, Full Color Flat Panel Display Technology Employing High Performance Crystalline Organic Semi Conductor Light Emitting Diodes," AFRL-HE-WP-TR-1998-0098, 44 pages (May 1998).

#### 3.1 Phosphorescent Dopants for OLEDs

##### 3.1.1 Iridium Complexes

Heavy metal complexes, particularly those containing Pt and Ir, can serve as efficient phosphors in organic light emitting devices. Both theoretical predictions and experimental measurements give a singlet-triplet ratio for these excitons of 1 to 3. Fluorescent materials typically used to fabricate OLEDs do not give detectable triplet emission (*i.e.* phosphorescence), nor is there evidence for significant intersystem crossing between the triplet and singlet manifolds at room temperature. The singlet-triplet ratio thus implies a limitation of 25% for the internal quantum efficiency for OLEDs based on fluorescence. By doping OLEDs with heavy metal phosphors, we have shown that the singlet-triplet limitation can be eliminated. The excited states generated by electron-hole recombination are trapped at the phosphor, where strong spin-orbit-coupling leads to singlet-triplet state mixing, and hence efficient phosphorescent emission at room temperature. Both singlet and triplet excited states can be trapped at the phosphor. OLEDs prepared with these heavy metal complexes are the most efficient OLEDs reported to date, with internal quantum efficiencies approaching 100% (photons/electrons) (> 19% external efficiency). We have developed a family of  $C^N_2Ir(LX)$  phosphor dopants ( $C^N$  = cyclometallating ligand, LX = ancillary bidentate ligand). The lowest energy (emissive) excited state in these  $C^N_2Ir(LX)$  complexes is a mixture of  $^3MLCT$  and  $^3(\pi-\pi^*)$  states. We have prepared roughly fifty different emitters, whose emission spectra range from blue to the near infra-red. All of these complexes have luminescent efficiencies between 0.20 and 0.75, with the majority being greater than 0.4. These dopants have been used to prepare efficient blue, green, yellow, orange and red emission. The external quantum efficiencies for these devices vary from 5 % to nearly 20 %. The green and red emissive devices have lifetimes > 20,000 hrs at display luminance representative of values in common hand held products (150-300 cd/m<sup>2</sup>).



### 3.1.2 Phosphorescent Cyclometalated Platinum Complexes

After the success we had with Ir based organometallic dopants, we chose to investigate Pt analogs of the complexes. The Pt complexes are square planar and it was not known if this would be deleterious in OLED emitter applications. The complexes had the general structure  $C^{\wedge}N Pt(O^{\wedge}O)$ , where  $C^{\wedge}N$  is a mono-anionic cyclometalating ligand and  $O^{\wedge}O$  is an  $\beta$ -diketonato ligand. Most of the  $C^{\wedge}N Pt(O^{\wedge}O)$  complexes display a single reversible reduction wave between  $-1.9$  to  $-2.6$  V, assigned to largely  $C^{\wedge}N$  ligand based reduction, and an irreversible oxidation, assigned to predominantly Pt based oxidation. DFT calculations were carried out on both the ground (singlet) and excited (triplet) states of these complexes. The HOMO levels are a mixture of Pt and ligand orbitals, while the LUMO is predominantly  $C^{\wedge}N$  ligand based. The emission characteristics of these complexes are governed by the nature of the organometallic cyclometalating ligand allowing the emission to be tuned throughout the visible spectrum. Twenty two different  $C^{\wedge}N$  ligands have been examined, which gave emission  $\lambda_{max}$  values ranging from 456-600 nm. Well resolved vibronic fine structure is observed in all of the emission spectra (room temperature and 77K). Strong spin-orbit coupling of the platinum atom allows for the formally forbidden mixing of the  $^1MLCT$  with the  $^3MLCT$  and  $^3\pi-\pi^*$  states. This mixing leads to high emission quantum efficiencies (0.02 – 0.25) and lifetimes on the order of microseconds for the platinum complexes. In general, the efficiencies of these emitters are too low to make them practical for OLED applications. The low luminescent yields are the result of oxygen quenching and aggregate induced self quenching. While these dopants were not suitable for monochromatic dopants they proved to be excellent for use in white OLEDs.

## 3.2 Electrode, Transport and Host Materials for OLEDs

### 3.2.1 Novel Amine Hole Transporting Materials

We have systematically explored a number of different diamine compounds. The goal was to determine what parameters are most important in determining how well a given material will perform as a hole transporter (HT). The synthesis of a series of asymmetric triaryl diamines has provided a number of materials with a wide range of thermal, electrochemical, and spectroscopic properties. The asymmetric materials have two different diaryl amine groups bound to a 1,4-phenylene or 4,4'-biphenylene core, *i.e.*  $Ar_1Ar_2N-C_6H_4-NAr_1'Ar_3$  or  $Ar_1Ar_2N$ -biphenyl- $NAr_1'Ar_3$  respectively. The diarylamines studied include diphenylamine, phenyl-*m*-tolylamine, naphthylphenylamine, iminostilbene, iminodibenzyl, and carbazole. The asymmetry inherent in these compounds prevents these low molecular mass compounds from crystallizing, thus yielding higher thermal stability over that of the symmetric derivatives. In all cases, the asymmetric diamines form stable glasses, with glass transition temperatures up to 125 °C. HOMO levels for these materials, estimated by cyclic voltammetry, show a broad range of values, with oxidation potentials both lower and higher than those of common hole transport materials used in organic light emitting diodes.

Out of the 60 diamine compounds prepared we chose eight to investigate in OLEDs. The diamines have  $T_g$  values ranging from 85 – 155°C. The lowest voltages and highest efficiencies are observed for iminostilbene containing diamines. These materials also have high  $T_g$  values, and long lived devices. Recently *bis*-iminostilbene-biphenyl (ISB) has been used in



electrophosphorescent devices, giving both high efficiency and long device lifetimes for green and red devices.

We have also examined a class of diamine hole-transporting materials (HTMs) based upon a fluorene core. Using a fluorene core, rather than a biphenyl group, leads to enhanced thermal stability, as evidenced by glass transition ( $T_g$ ) temperatures as high as 161°C for N-N'-iminostilbenyl-4,4'-fluorene (ISF). The fluorene based HTMs have lower ionization potentials ( $I_p$ ) than their biphenyl analogs, which leads to more efficient injection of holes from the ITO anode, and higher quantum efficiencies. Devices prepared with fluorene based HTMs were operated under thermal stress. The failure of an OLED under thermal stress has a direct correlation with the thermal stability of the HTM that is in contact with the ITO anode. OLEDs based on ISF are stable to over 140°C.

### 3.2.2 1,8-Naphthalimides in Phosphorescent OLEDs:

#### Interplay Between Dopant, Exciplex and Host Emission

While the search for new hole transporters (HTs) has led to marked enhancements in both the thermal excitons and hole excitons in HTLs, similar advances have not been observed for ETLs. Alq<sub>3</sub> was introduced in the first efficient OLEDs and has remained the most heavily studied and efficient ET. Alq<sub>3</sub> combines a high thermal stability with good electron mobility and a moderately wide energy gap. Proposed replacements include molecules such as oxadiazoles, triazoles and other metal quinolates. While these materials have wider energy gaps than Alq<sub>3</sub>, they all suffer from poor electrical properties and thermal stabilities relative to Alq<sub>3</sub>. As potential ET materials we have investigated naphthalimides. These materials have demonstrated high electron mobilities in organic transistor structures. Four different 1,8-naphthalimide derivatives were examined in phosphorescent organic light emitting diodes (OLEDs). Photoluminescence from all four naphthalimides have violet-blue fluorescence and phosphorescent bands between 550 and 650 nm (visible at 77K). While all four compounds gave good glassy films when doped with a phosphorescent dopant, only the niBr (N-2,6 dibromophenyl-1,8-naphthalimide) films remained glassy for extended periods. OLED studies focused on niBr, with two different architectures. One OLED structure (type 1) had the niBr layer as a doped luminescent layer and an undoped niBr layer to act as a hole blocking layer. The alternate structure (type 2) utilizes a doped CBP layer as the luminescent layer and the niBr layer is used as a hole blocking layer only (CBP = 4,4'-N,N'-dicarbazolyl-biphenyl). Type 1 and 2 OLEDs were prepared with green, yellow and red emissive phosphorescent dopants (Irppy, btlr and btpIr, respectively). The dopants were organometallic Ir complexes, previously shown to give highly efficient OLEDs. Of the three dopants, the btpIr based OLEDs showed the best device performance in both structures (peak efficiencies for type 2: 3.2 % and 2.3 lm/W at 6.3 V; type 1: 1.7% and 1.3 lm/W at 6.1 V). The green and yellow dopants gave very similar performance in both type 1 and 2 devices (peak efficiencies are 0.2-0.3%), which were significantly poorer than the btpIr based OLEDs.

The emission spectrum of the btlr and btpIr based devices (type 1 and 2) are the same as the solution photoluminescence spectrum of the dopant alone, while the Irppy device gives a broad red emission line ( $\lambda_{max}$  = 640 nm). The red Irppy-niBr emission line is assigned to an Irppy-niBr exciplex. The type 2 Irppy based device gave a voltage dependent spectrum, with the red

emission observed at low bias (4-8 V), switching over to strong green emission as the bias was raised. All other devices showed bias independent spectra. Estimates of HOMO, LUMO and excited state energies (dopant, niBr and exciplex) were used to explain the observed spectral properties of these devices. BtpIr based devices emit efficiently from isolated dopant states (external efficiencies = 3.2 %, 2.3 lm/W). Irppy based devices emit only from exciplex states, with low efficiency (external efficiency = 0.3 %). BtIr-niBr films have very similar energies for the dopant, exciplex and niBr triplet states, such that relaxation can go through any of these states, leading to low device efficiency (external efficiency = 0.4 %). High device efficiency is only achieved when dopant emission is the dominant pathway for relaxation, since exciplex and niBr triplet states give either weak or no electroluminescence.

### 3.2.3 Cyclooctatetraene Electron Transporting Materials

We have also investigated cyclooctatetraene ET materials ( $C_8R_8$ ). The derivatives with R = aryl have high thermal stabilities and wide energy gaps. The aryl groups should give good intermolecular electrical contact and thus high carrier mobility. Part of this project involved the development of novel synthetic routes into these materials, since only a few such molecules were known and their synthesis was not straightforward. Tetraaryl-tetraarylethynyl-cyclooctatetraenes [ $C_8Ar_4(C\equiv Car)_4$ ] were prepared from diaryldiynes with a metal catalyst in good yield (40-80%). Octaaryl-cyclooctatetraenes (COTS) were prepared from diarylacetylenes by treatment with lithium and iodine in 50% yield. Cyclic voltametry indicates that these COTs are reduced in sequential one electron steps.  $C_8Ar_4(C\equiv Car)_4$  and  $C_8Ar_8$  are thermally stable to sublimation and have wide optical energy gaps [ $\lambda_{max}$  (emission) = 392-412 nm] making them good candidates for use in organic LEDs. These octasubstituted COTs have been used as electron transport layers in single heterostructure organic LEDs, *i.e.* ITO/NPD 400 Å/COT 400 Å/Mg-Ag (ITO = indium-tin-oxide, NPD = N,N'-diphenyl-N,N'-dinaphthylbenzidine). External quantum efficiencies of 0.1-0.2 % (photons/electrons) were observed, with turn-on voltages with a calculated value of (*ca.*) 6 V. The emission from this device comes exclusively from the NPD hole transporting layer, with a  $\lambda_{max}$  of 435 nm. Doping the NPD layer with 1% perylene leads to an increased quantum efficiency of 0.6% and an electroluminescence spectrum indicative of emission solely from the perylene dopant, confirming exclusive emission from the NPD hole transporting layer. The turn-on voltage for this devices was 4 V and the efficiency is near the theoretical limit for HT doped devices, demonstrating that the cyclooctatetraenes make an excellent new family of ET materials.

### 3.2.4 Vacuum Deposition of Thin Films of Pentaphenylcyclopentadienyl Radical

We have examined the preparation and morphology of the films of 1,2,3,4,5-pentaphenylcyclopentadienyl radical ( $Cp^{5\phi\bullet}$ ). The electron in  $Cp^{5\phi\bullet}$  is delocalized over the cyclopentadiene ring, giving the free radical and anionic forms of  $Cp^{5\phi\bullet}$  similar structures, and thus a potentially low polaron binding energy. Open shell molecules have never been examined in organic electronic applications. Thin films of 1,2,3,4,5-pentaphenylcyclopentadienyl radical ( $Cp^{5\phi\bullet}$ ;  $\phi = C_6H_5$ ) were obtained upon decomposition of decaphenylplumbocene [ $PbCp^{5\phi}_2$ ] in vacuo. Formation of the radical species was confirmed by EPR as well as electron absorption and emission spectroscopy.  $Cp^{5\phi\bullet}$  decomposes slowly in solution, which is accelerated by aerobic exposure. Methods of protecting the thin films of  $Cp^{5\phi\bullet}$  from aerobic decomposition were

developed and used to protect the films during handling and microscopic analysis. Unfortunately, the air sensitivity of these materials precluded any further study in OLED structures.

### 3.2.5 TiN as an Anode Material for OLEDs

Most OLEDs have been fabricated with ITO anodes. While this material is readily available and easily patterned using wet chemical etching techniques, it is not stable over long periods. Several groups have shown that the ITO reorganizes, giving  $\text{SnO}_2$  features that grow out of the ITO film, ultimately shorting the device. We have investigated the use of alternate materials as anodes for OLEDs. One particularly promising material is TiN. This material has metal like conductivity and is a refractory material, making it stable toward restructuring over long periods of time. Highly conductive thin films of TiN were prepared on glass substrates by metal organic CVD, using  $\text{Ti}(\text{Nme}_2)_4$  and  $\text{NH}_3$ . The sheet resistances of these films decreased with increasing film thickness, with a 230 Å film giving a sheet resistance of  $190 \Omega/\square$ , comparable to ITO. The thin films have good transparency (70-80% transparent), while the thicker films are opaque (films > 600 Å have transmittance < 10%). TiN films in thicknesses ranging from 35 Å to 180 Å were used as anodes in small molecule based organic LEDs (anode/ $\alpha$ -NPD/ $\text{Alq}_3$ /Mg-Ag). These OLEDs showed good external quantum efficiencies (0.2 – 0.44 %), comparable to OLEDs fabricated with indium tin oxide (ITO) anodes. Thin films of TiN coated on top of ITO, stabilized the ITO anode and gave OLEDs with efficiencies superior to ITO.

## 3.3 Molecularly Doped Polymer OLEDs

Fluorescent dopants have been used in both small molecule and polymer based OLEDs. The dopants enhance efficiency by trapping and acting as radiative centers for excitons. We have demonstrated that the use of phosphorescent dopants led to a marked increase in efficiency. We chose to look at the use of phosphorescent dopants in polymer OLEDs to see if it is possible to enhance the efficiencies of polymer OLEDs by harvesting both singlet and triplet excitons. The use of molecular phosphorescent dyes in polymer-based organic light emitting diodes of different architectures was investigated by incorporating several phosphorescent dopants into PVK-based single-layer and single heterostructure LEDs. The maximum external quantum efficiency of phosphorescent devices exceeds 0.6% for PtOEP and organometallic Pt dopants and reaches ca. 5.5% for organometallic Ir complexes. An overall increase in LED efficiency compared to similar devices based on fluorescence is attributed to the fact that phosphorescent dopants allow both singlet and triplet excitons to be involved in emission. In addition to finding an energetically suitable dopant, such parameters as dopant concentration and organic layer thickness influence the performance of the LEDs. The second order quenching process present in these OLEDs, which is prevalent at high current densities, is most likely not due to T-T annihilation of excitons trapped at dopant sites in these OLEDs. T-T annihilation in the PVK matrix or trapped charge-triplet annihilation are more likely explanations for the decrease. To maximize the efficiency of these doped devices electron-transporting materials should be used not only in the form of a thin vacuum deposited layer (forming the heterostructure), but also as a component blended in the PVK thin film. Moreover, the hole-blocking ability of BCP in the PVK-based electrophosphorescent devices allows for further LED architecture modifications and improvements. While PVK has been examined extensively in mdpLED structures, it may not be

the optimal polymer for this application. A useful approach to improve the performance of mdpLEDs is to explore other polymeric host materials with phosphorescent dopants.

### 3.4 High Efficiency Single Dopant White Electrophosphorescent OLED (WOLED)

#### 3.4.1 Double Dopant WOLEDs

The pace of research in the search for new white light sources has recently seen a marked increase in response to the need for more efficient and environmentally friendly solutions to the impending energy shortage. Among methods for producing white light, electrophosphorescence stands out as the most effective mechanism for OLED emission due to its demonstrated potential for achieving 100% internal emission efficiency. While electrophosphorescence, typically achieved by doping an organometallic phosphor into a conductive host, has successfully been used to generate the primary colors necessary for display applications, efficient generation of the broad spectral emission required of a white light source has remained elusive.

We have demonstrated a general solution to the problem of efficient white light generation in organic light emitting devices, using the novel process of phosphor excimer emission. These electrophosphorescent organic light emitting devices solve the problem of interactions between multiple dopants for the generation of white light by using a single phosphor for blue emission, as well as for forming excimers that emit from green to red. Energy transfer between dopants (leading to current-dependent color changes) is significantly reduced since excimers lack a bound ground state, thus offering a simplified means to achieve broad spectral emission from organic light emitting devices. This approach is well suited to low cost white light emitters which eventually might replace existing, illumination sources. Using two phosphor dopants, devices with a high color rendering index of 78, a maximum external quantum efficiency of  $\eta_{\text{ext}} = (4.0 \pm 0.4)\%$  corresponding to  $(9.2 \pm 0.9)$  cd/A, and a maximum luminance of  $(31,000 \pm 3,000)$  cd/m<sup>2</sup> at 16.6V, demonstrate that efficient and bright electrophosphorescent white organic light emitting devices based on excimer emission can significantly exceed efficiencies of fluorescent white light emitters based on this same principle.

#### 3.4.2 Single Dopant WOLEDs

Efficient white electrophosphorescence has been achieved with a single emissive dopant. The dopant in these WOLEDs emits simultaneously from monomer and aggregate states, leading to a broad spectrum and high quality white emission. The dopant molecules are based on a series of platinum (II) (2-(4,6-difluorophenyl)pyridinato-N,C<sup>2'</sup>)  $\beta$ -diketonates. All of the dopant complexes described herein have identical photophysics in dilute solution with structured blue monomer emission ( $\lambda_{\text{max}} = 468, 500, 540$  nm). A broad orange aggregate emission ( $\lambda_{\text{max}} \approx 580$  nm) is also observed, when doped into OLED host materials. The intensity of the orange band increases relative to the blue monomer emission, as the doping level is increased. The ratio of monomer to aggregate emission can be controlled by the doping concentration, the degree of steric bulk on the dopant and by the choice of the host material. A doping concentration where the monomer and excimer bands are approximately equal gives an emission spectrum closest to standard white illumination sources. WOLEDs have been fabricated with doped CBP and mCP luminescent layers (CBP = N,N'-dicarbazolyl-4,4'-biphenyl, mCP = N,N'-dicarbazolyl-3,5-benzene). The best efficiencies and color stabilities were achieved when an electron/exciton

blocking layer (EBL) is inserted into the structure, between the hole transporting layer and doped CBP or mCP layer. The material used for an EBL in these devices was *fac*-tris(1-phenylpyrazolato,N, C<sup>2'</sup>)iridium(III). The EBL material effectively prevents electrons and excitons from passing through the emissive layer into the hole transporting NPD layer. CBP based devices gave a peak external quantum efficiency of  $3.3 \pm 0.3\%$  ( $7.3 \pm 0.7$  lm/W) at  $1 \text{ cd/m}^2$ , and  $2.3 \pm 0.2\%$  ( $5.2 \pm 0.3$  lm/W) at  $500 \text{ cd/m}^2$ . mCP based devices gave a peak external quantum efficiency of  $6.4\%$  ( $12.2$  lm/W,  $17.0 \text{ cd/A}$ ), CIE coordinates of  $0.36 \ 0.44$ , and a CRI of  $67$  at  $1 \text{ cd/m}^2$  (CIE = Commission Internationale de l'Eclairage, CRI = color rendering index). The efficiency of the mCP based device drops to  $4.3 \pm 0.5 \%$  ( $8.1 \pm 0.6$  lm/W,  $11.3 \text{ cd/A}$ ) at  $500 \text{ cd/m}^2$ , however, the CIE coordinates and CRI remain unchanged.

### 3.5 OLED Reliability

Based on the world-record efficient electrophosphorescent OLED (PHOLED) device design invented by our team, UDC lead the reliability effort to develop materials and device structures to meet the lifetime specifications for a full-color display application. A 225 channel custom life test system was designed and built. An optically transparent package for OLEDs was designed and built to provide >10,000 hrs shelf life. Operational lifetimes of >10,000 hrs at luminance levels required for display products were demonstrated for both green and red phosphorescent OLEDs (PHOLED). Detailed test results are as follows:

- Red PHOLED at CIE= (0.71,0.29), LE= 3 cd/A at 100 cd/m<sup>2</sup>,  
Lifetime > 10,000 hrs at 100 cd/m<sup>2</sup>
- Red PHOLED at CIE= (0.65,0.34), LE= 11cd/A at 300 cd/m<sup>2</sup>,  
Lifetime > 10,000 hrs at 300 cd/m<sup>2</sup> which corresponds to 30,000 hrs at 100 cd/m<sup>2</sup>
- Green PHOLED at CIE= (0.28,0.64), LE= 23 cd/A at 600 cd/m<sup>2</sup>,  
Lifetime > 10,000 hrs at 600 cd/m<sup>2</sup> which corresponds to 60,000 hrs at 100 cd/m<sup>2</sup>

### 3.6 Display Prototypes

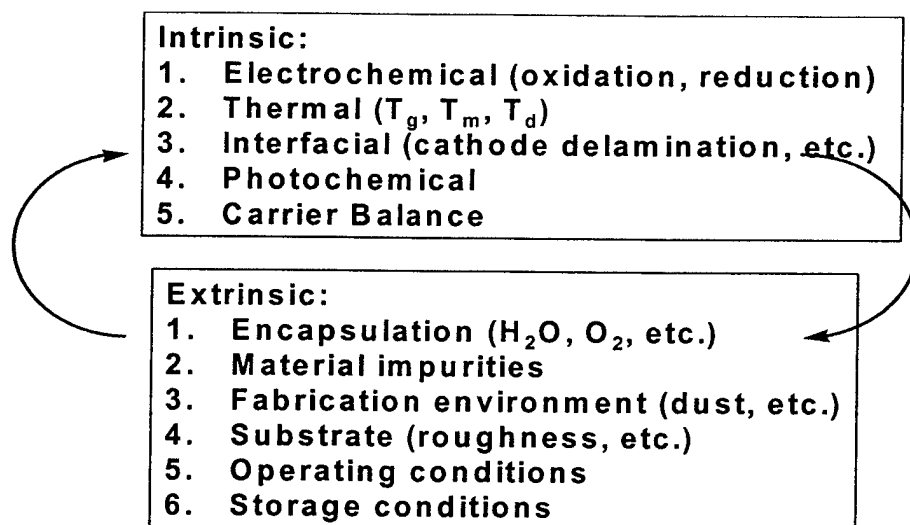
Three “world’s first” display prototypes were designed and fabricated at UDC based on three OLED device platforms invented by the Princeton University team:

- Transparent OLED, or TOLED. This demonstration was the world’s first optically transparent passive matrix OLED display.
- Flexible OLED, or FOLED. This demonstration was the world’s first flexible passive matrix OLED display.
- Multi-color display prototype based on the phosphorescent or PHOLED. This demonstration proved to the community that PHOLEDs were a superior device technology for OLEDs as compared to conventional fluorescent emitters.

These prototypes were produced after three steps were accomplished to transition the technology to commercial use. These same three steps are on the critical path to providing the military, a high-performance niche-market customer, access to a low cost, commercial source for OLED displays. First, Princeton University and USC entered an agreement with UDC for UDC to hold and commercialize the OLED intellectual property (patents, know-how) developed at Princeton and USC. Second, to accomplish display prototyping and low-volume work, and to develop large-scale production know-how, UDC designed and built a 10,000 sf Pilot Line Facility in Ewing NJ in proximity to Princeton University. The grand opening for this facility was in December, 1999. Third, UDC assembled a world-class research and development team to perform the development work required to commercialize OLED technology developed at PU, USC, and UDC.

### 3.7 OLED Process Technology and Reliability

There are a number of inter-relating factors that affect OLED device lifetime. The factors can be separated into extrinsic and intrinsic reliability drivers (see below).



**Figure 3:** Eleven intrinsic and extrinsic factors determining reliability of an OLED display

At the start of this program the challenge was to develop OLED processing and encapsulation techniques to minimize the extrinsic factors so that we could then focus on the device materials and structure affects on lifetime (i.e. intrinsic factors). There have been many proposed mechanisms for the decay in luminance, but most theories agree that a dominant degradation mechanism is exposure of the OLED to atmospheric oxygen and water. This leads to oxidation and delamination of the metal cathode as well as chemical reactions within the organic layers. The visible degradation effect on the OLED is the appearance of “dark spot” defects or non-emissive regions. In addition, the pixel active area may shrink by degradation at the device periphery. So, our first task was to develop a glass-to-glass encapsulation process (Figure 4) to reduce the degradation due to exposure to moisture. Towards this end we developed a process to seal a glass lid to the glass substrate with a precision controlled bead of UV cured epoxy resin. A desiccant such as calcium oxide was also incorporated into the package to react with any residual water incorporated in the package or diffusing through the epoxy seal. The results are shown in Figures 4. Prior to package optimization, the OLED device was severely degraded due to dark spot growth after only 4,000 hrs of life testing as shown in Figure 4(b). We were able to significantly extend the lifetime of the package by optimizing the choice of UV epoxy resin and incorporating the dessicant. A photograph of the packaged OLED at  $t=0$  and  $t=10,000$  hrs is shown in Figures 4(c) and 4(d.) Based on this process we then proceeded to study the intrinsic OLED device design to extend the operational lifetime to  $> 10,000$  hrs.

In order to achieve this goal, we considered the affect of device design on reliability. The first factor we considered was materials. Device lifetimes can be strongly related to the choice of the

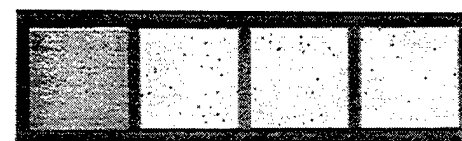
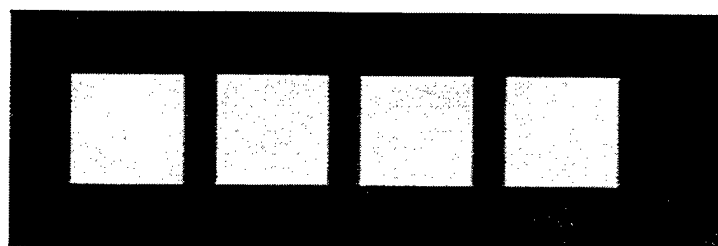
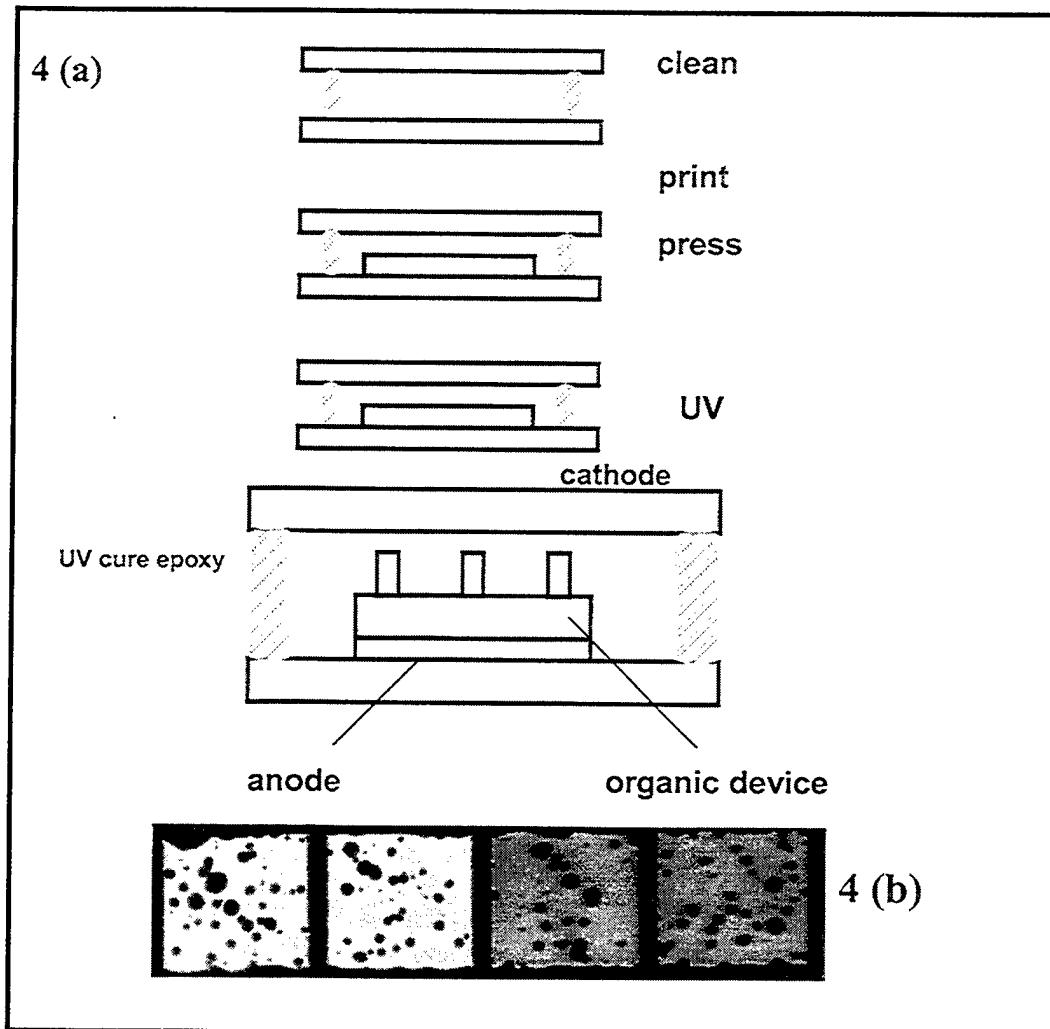
materials used in their construction. The most efficient devices are composed of multiple layers, serving different functions, *i.e.*, hole transporting, emitting, blocking and electron transporting layers. The lifetimes of green emitting Ir(ppy)<sub>3</sub> doped OLEDs are strongly dependent on the choice of blocking material. The Ir(ppy)<sub>3</sub> based devices employing a 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) hole blocking layer gave low stability, with half-lives ( $T_{1/2}$ ) less than 700 hrs at initial luminances ( $L_0$ ) of 600-1200 cd/m<sup>2</sup> whereas devices employing a aluminum(III)bis(2-methyl-8-quinolinato)4-phenylphenolate (BALq) hole blocking layer gave high stability, with  $T_{1/2}$  approaching 4000 hrs at  $L_0$  of ~570 cd/m<sup>2</sup>. This work has been reported first by Watanabe et. al. from Pioneer and our research team. Based on these results, we have examined a number of different blocking materials, in an effort to improve the device lifetime.

All devices in this study were fabricated by high vacuum ( $10^{-8}$  Torr) thermal evaporation. The active area of each test pixel was 5 mm<sup>2</sup>. The devices consisted of an ITO anode, 100 Å of copper phthalocyanine (CuPc) as the hole injection layer, 300 Å of 4,4'-bis[N-(1-naphthyl)-N-phenylamino]biphenyl ( $\alpha$ -NPD) as the hole transporting layer, 300 Å of 4,4'-bis(N-carbazolyl)biphenyl (CBP) doped with 6% of Ir(ppy)<sub>3</sub> as the emissive layer, 100 Å of a hole blocking layer, 400 Å of tris(8-hydroxyquinolato)aluminum (Alq<sub>3</sub>) as the electron transporting layer. The cathode was comprised of 10 Å of lithium fluoride followed by 1,000 Å of aluminum. All devices were encapsulated in a nitrogen glove box (<1 ppm of H<sub>2</sub>O and O<sub>2</sub>) immediately after device fabrication with a glass lid as the cover and an epoxy resin as the sealant. A calcium oxide based moisture getter was incorporated inside each packaged device (as described above). By careful device and materials optimization we have improved the lifetime over the course of this program (see Figure 5). We have continued this work funded, in part, by additional government programs and today have achieved commercial specifications for both the green and red PHOLEDs. A summary of the combined lifetime and device efficiency is given in Table I. These results represent a world record for combined efficiency and lifetime.

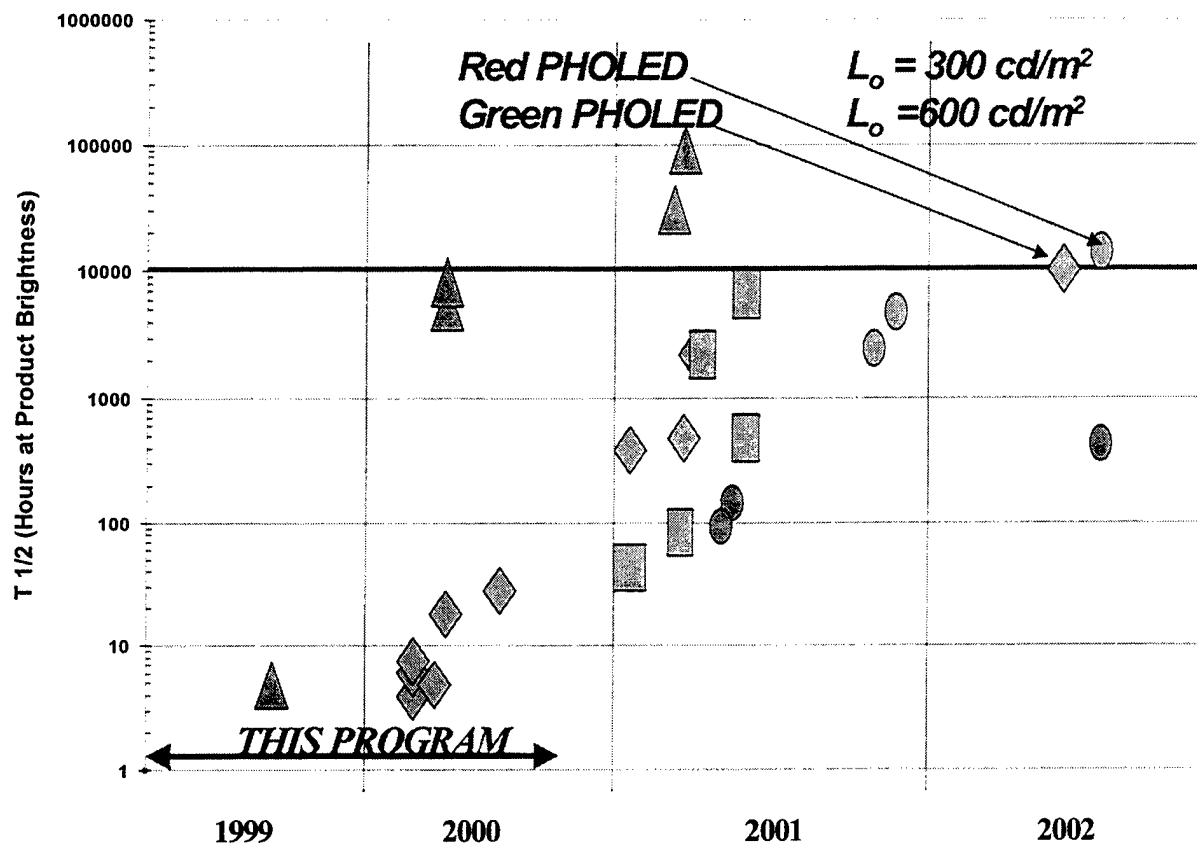
**Table I:** Summary of a sub-set of phosphorescent OLED performance.

EL color	Deep red	Red	Blue	Green
Peak wavelength (nm)	650	620	474	510
CIE - x	0.71	0.65	0.16	0.28
CIE - y	0.29	0.35	0.32	0.64
Luminance eff @ 1 mA/cm <sup>2</sup> (cd/A)	1.0	11	11	24
Lifetime (hours)	100,000 @ 70 cd/m <sup>2</sup>	15,000 @ 300 cd/m <sup>2</sup>	Under development	10,000 @ 600 cd/m <sup>2</sup>





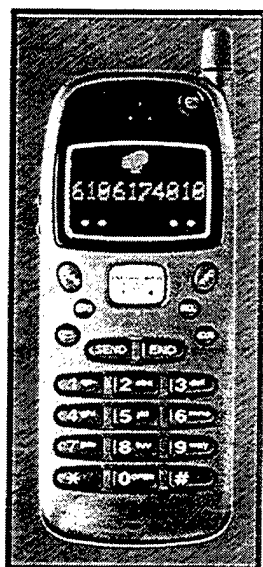
**Figure 4:** OLED packaging. (a) OLED packaging process flow developed to improve encapsulation for long term reliability. At start of program the reliability was limited due to dark spot defect growth as illustrated in the photograph (b) at  $t=4,000$  hrs. After the package development, the shelf life of the package is significantly improved. A photograph of an encapsulated green PHOLED at (c)  $t=0$  and (d)  $t=10,000$  hrs demonstrates the integrity of the package (i.e. minimal dark spot growth or pixel shrinkage).



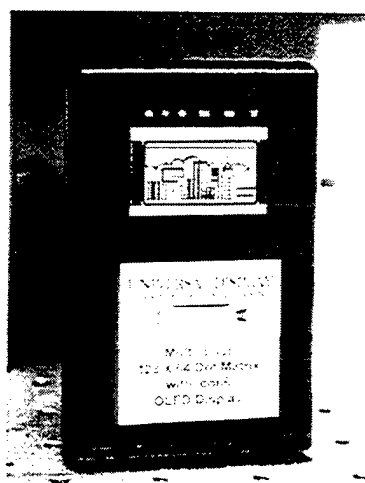
**Figure 5:** Summary of progress made in increasing the operational lifetime for our phosphorescent OLED technology since 1999. The lifetime values reported in this chart are for initial luminance values (i.e.  $L_o$ ) required for full-color active matrix display applications. The red PHOLEDs are reported at  $L_o=300 \text{ cd/m}^2$ , green PHOLEDs at  $L_o=600 \text{ cd/m}^2$  and blue PHOLEDs at  $100 \text{ cd/m}^2$ . The red and green PHOLED performance meets display product requirements; they are ready for commercial applications.

### 3.8 Engineering Prototypes

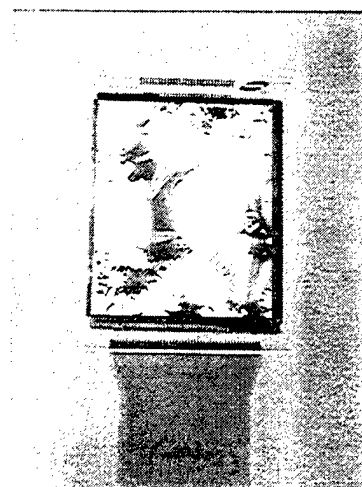
During the course of the program we developed display prototypes based on three OLED design platforms: (a) passive matrix display using phosphorescent OLEDs (PHOLEDs), (b) passive matrix display using transparent OLEDs (TOLEDs) and (b) passive matrix display using flexible OLEDs (FOLEDs). Since the completion of this program we have continued the development of these three display designs. Photographs and description of the work under this program and today's status are shown below in Figures 6, 7, 8, 9, and 10.



**First Display Prototype:** Multi-color static addressed display using phosphorescent red OLED and undoped green and blue OLEDs. This display was fabricated in the Princeton University Laboratory and installed into a commercial cell phone module (1999). Built during this program



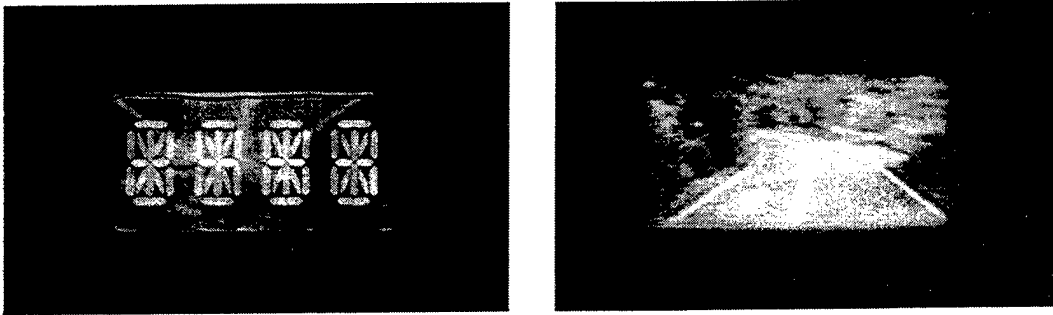
**First Passive Matrix Display Prototype:** Multi-color passive matrix display fabricated with phosphorescent green and red OLEDs. This display was fabricated in UDC's Pilot Line Facility. The matrix portion of the display is 128 x 64 pixels with a density of 60 pixels/in. Built during this program in 2000.



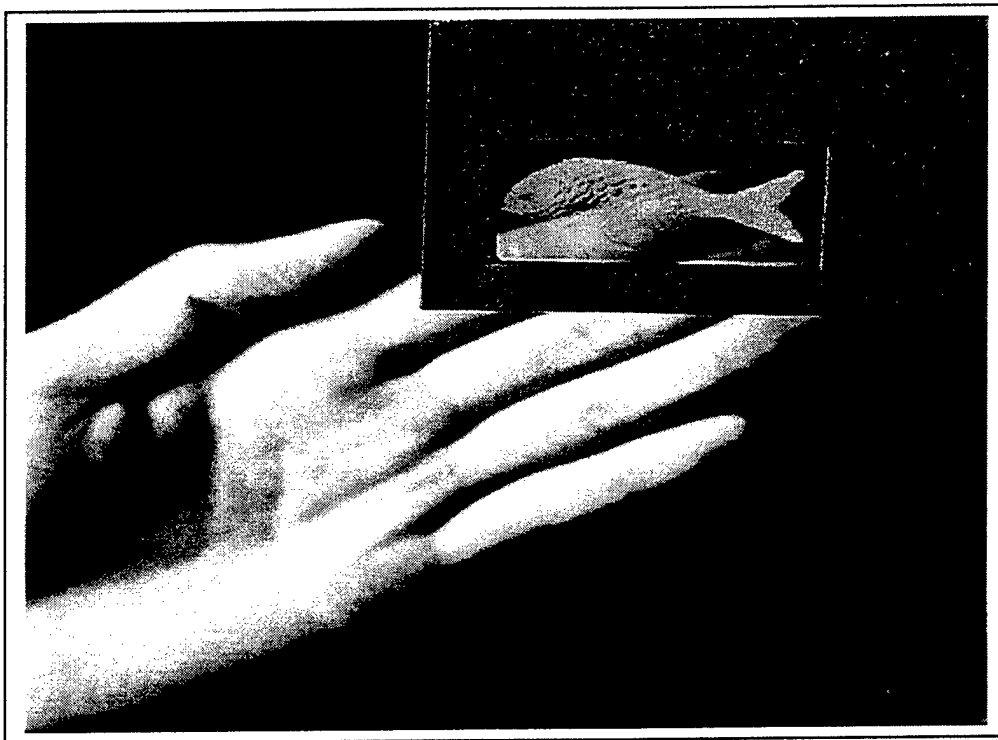
**Active Matrix OLED Display Using Red & Green PHOLEDs:**  
2.2 in. Diagonal Display by Samsung SDI .

PARAMETER	SPECIFICATION
Diagonal size	2.2 in.
No. of pixels	176 (H) x RGB x 220(V)
Pixel pitch ( $\mu\text{m}$ )	66 x 198
Pixel Density	128 pixels/in.
Panel size (mm)	41.976 (H) x 56.232 (V)
Aperture ratio	32%
Luminance (w/o polarizer)	200 cd /m <sup>2</sup> Peak: >300 cd /m <sup>2</sup>
White point	(0.31,0.32)

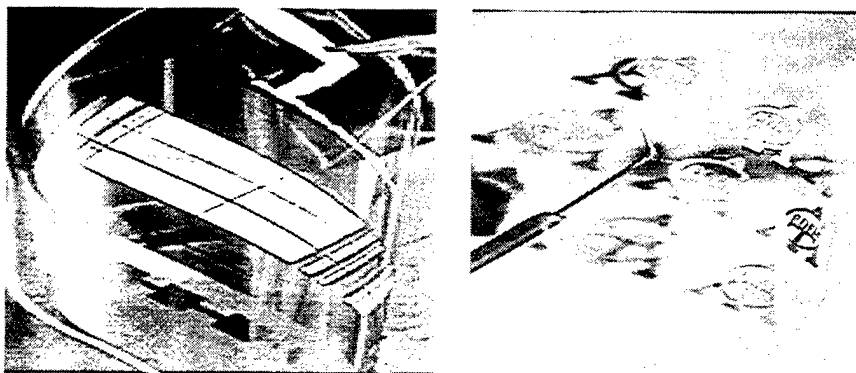
**Figure 6:** Phosphorescent OLED engineering prototype displays enabled by this program.



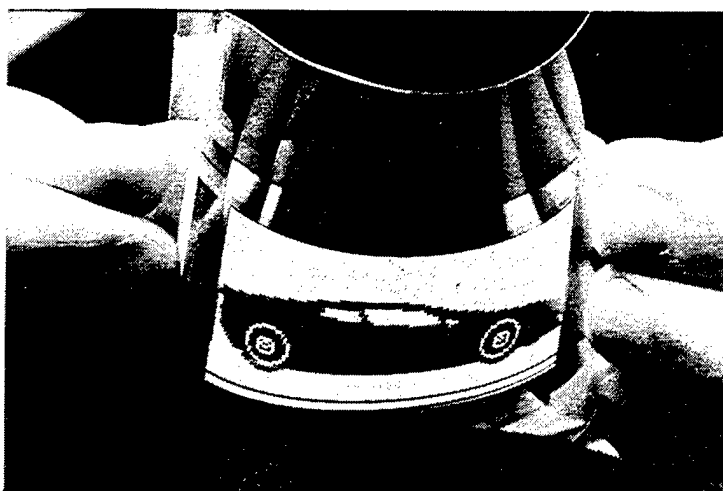
**Figure 7:** Display prototype built using the novel transparent OLED (or TOLED) design. This matrix addressable TOLED display demonstrates the application of integrating the display into a car windshield with information displayed when addressed (left hand picture) and becoming optically transparent when turned off (right hand picture). Built during this program in 1999.



**Figure 8:** TOLED passive matrix display prototype fabricated with red phosphorescent OLED in 2002.



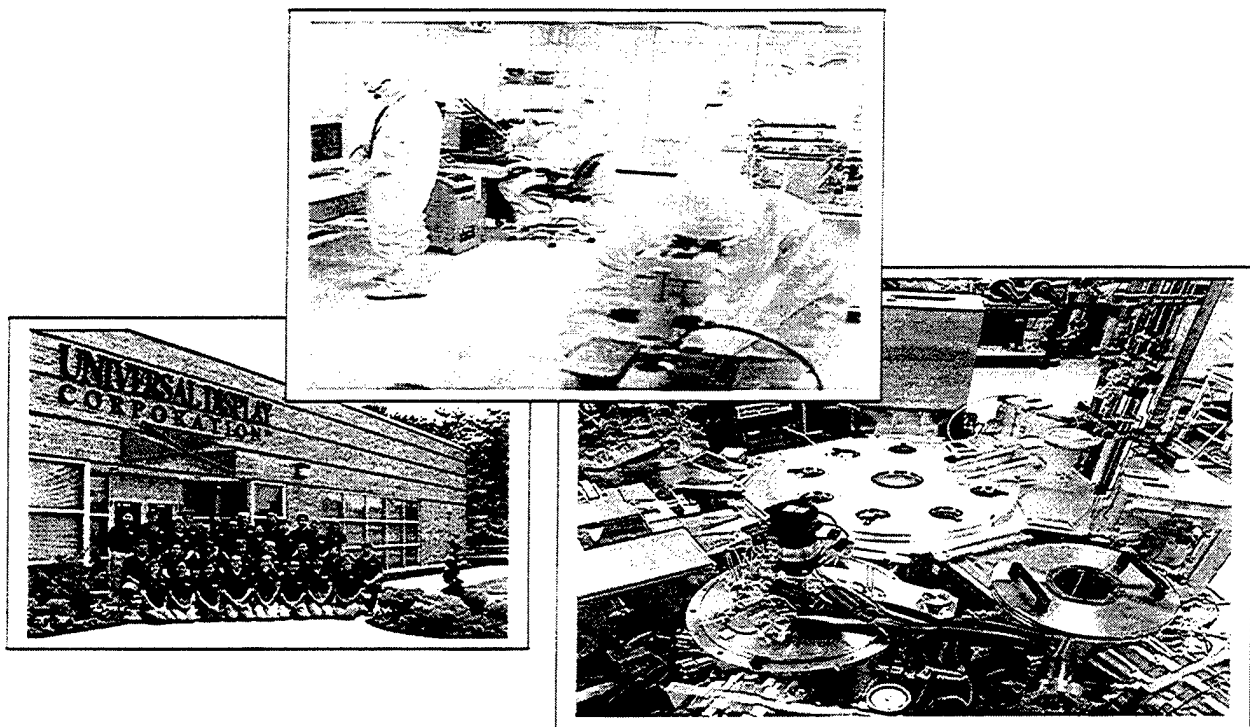
**Figure 9:** First flexible display prototypes built by our team. Icon flexible OLED (FOLED) Display (right hand picture) built on PET substrate--represented the world's first flexible small-molecule OLED demonstration. The team started to work on further developing this technology and under this program funding built a partially functioning passive matrix FOLED display (left hand side).



**Figure 10:** World's first functional passive matrix OLED Display. Developed by UDC based on work accomplished under this grant by PU, USC, and UDC.

### 3.9 Pilot Line Plant Design

In September of 1999 we completed the construction of our Pilot Line Facility located at 375 Phillips Blvd in Ewing, New Jersey. By the end of the year we had completed the first phase of equipment installation to run our 4" substrate line. By the end of the second year we had completed the installation of our 6" substrate line. This facility provides UDC with infrastructure to complete its product and process technology transfer packages for full-scale production and product development. Furthermore, the UDC technical staff will use the new facility to accelerate the transfer of academic innovation into display product prototypes. Specifically, the Facility will satisfy several key objectives: (a) engineering and commercial prototype fabrication, (b) continued device and process optimization, (c) manufacturing scale-up, and (d) process and product reliability validation. The pilot line is designed to produce several hundred displays per month, up to 6 x 6 in. It contains materials purification, substrate (i.e. both glass and plastic) preparation, photolithography, vacuum deposition, packaging and metrology labs within Class 100 and 100,000 clean room environments. The Facility also has support capabilities including optoelectronic testing, quality control, reliability, and prototype assembly laboratories. This 11,000 sq. ft. facility, located not far from Princeton University, serves as a technology transfer center for commercial partners and UDC's corporate headquarters. Today, we have now further expanded this Pilot Line to 21,000 sq. ft. to further expand our capability. Photographs of our team and some of the laboratories are shown below:



**Figure 11.** Universal Display OLED prototyping facility in Ewing NJ.

### 3.10 Flexible AM Backplane Displays

#### 3.10.1 First Phase Backplane Research

The first phase of this program (1994-1997) involved development of multi-color organic light-emitting devices (OLEDs) and of multi-element OLED arrays. HRL Laboratories focused on the development of the multi-pixel arrays. First, HRL successfully learned the technology of fabricating organic light-emitting devices (OLEDs) from Princeton University. After that, HRL made numerous improvements to the OLED and demonstrated several novel displays. These displays include alphabetic logos and multiple-pixel arrays with emission from one face or from both faces (semi-transparent devices). HRL also constructed facilities to perform reliability testing of OLEDs, which would be supplied to HRL by Princeton. Highlights of these accomplishments are described below.

The HRL effort on the OLED fabrication improvement and array-display development was performed primarily in the first year. The accelerated pace was adopted in order to capture marketing opportunities and to ensure the continued leadership position of our team in the rapidly advancing area of OLED technologies. HRL first evaluated several samples of discrete OLEDs fabricated at Princeton. As a result of these evaluations, HRL focused our efforts on making several specific improvements to the OLEDs. These efforts were intended to produce a more manufacturable approach to the fabrication of devices.

Since HRL did not have the facilities for depositing thin films of organic materials, fabrication of the OLEDs by HRL included processing steps done at HRL as well as at Princeton. The basic OLED contained layers of ITO (the anode), an insulator (for some designs), organic materials comprising of the hole-transporting, electroluminescent, and electron-transporting layers, the MgAg cathode, and a covering conductor (either Ag or ITO). The ITO and insulator layers were processed at HRL. The organic materials, cathode and covering conductor were deposited at Princeton. After these layers were deposited, a glass cover piece was placed over the sample and sealed along its perimeter by an adhesive, to enclose the reactive OLED materials.

HRL fabricated over 130 samples and made 9 trips to Princeton for the device processing steps. As a result of this extensive effort, we identified various improvements to the OLED structure and fabrication process. We made improvements in reducing the series resistance, reducing the operating voltage, reducing the likelihood of short or open circuits, and increasing the integrity of contact pads. We reduced the series resistance by increasing the thickness of the Ag covering conductor from 50 nm to 150-200 nm. This additional covering also improved the long-term integrity of the MgAg contact by protecting it from corrosion. To improve the contact pads, we deposited a metal such as Ag or Au over the anode contact pad areas so that the electrical connection need not be made to the ITO. Such pads are amenable to wire bonding and are resistant to scratching. We reduced the operating voltage by carefully controlling the Mg to Ag ratio of the cathode and by ensuring that the deposition is done in a high vacuum. We also limited the exposure of the ITO anode surface to high temperatures, reactive gases and chemical etchants. We reduced the likelihood of electrical shorts and opens by adjusting the layer thicknesses and patterning methods.

HRL investigated several different sealants in an attempt to improve the shelf life and operating lifetime of OLEDs. We identified 4 different materials, all low-outgassing epoxies and vacuum sealants, and compared them with the sealant used by Princeton. Two of the sealants - epoxies from TraCon and EpoTek - demonstrated operation lifetimes that were at least as good as the results obtained with the Princeton sealant, another EpoTek epoxy. However, examination of samples sealed with those 3 sealants showed dark spots development after 6 months of storage.

HRL designed and fabricated several types of OLED samples. One type, used for comparing process and design modifications and for lifetime tests, contains 4 separate OLEDs that were separately addressed. A maximum of 4 samples could be processed in a single fabrication run. This permitted us to make side-by-side evaluations of processing parameters and test conditions. A second type of sample contained alphabetic displays of Hughes and Delco logos. We found these samples of great use in marketing the OLEDs. We demonstrated "standard" displays, for which the light is emitted through the glass substrate. We also demonstrated semi-transparent displays, for which the light is also emitted through the cathode contact. As an example of the effectiveness of our collaboration with Princeton, HRL successfully demonstrated a first-ever transparent logo display shortly after Princeton demonstrated the first transparent OLEDs. We then suggested process improvements that aided Princeton to demonstrate the first-ever, transparent 11-segment alphanumeric displays.

HRL established a fixed, basic design for the size of test samples and for the contact-electrode patterns on those samples. This permitted us to use machined fixtures and interchangeable masks in the device fabrication as well as simple contact pins and clamps in the test setups and demonstration units. The OLED samples were 0.75 x 0.75 in. in size and had a light-emitting area as large as 0.4 x 0.4 in. The sample size was selected to make them compatible with the display evaluation setups at GM/Delco Electronics (now Delphi Automotive Systems).

One goal in the first phase of the program was the development of an 8x8 pixel, 3-color display by the Princeton/Hughes/USC team. The HRL effort focused on a single-color array and demonstrated single-color (green) 8x12 pixel displays. In contrast to the row-and-column addressed displays reported initially by Pioneer, these displays had separate connections for each pixel. Since each illuminated element of the display had power applied continuously rather than being scanned, the instantaneous drive power to each pixel could be much lower. Furthermore, our design can be extended simply to versions that contain integrated driving and switching electronics. The displays we demonstrated had 400x400  $\mu\text{m}$  pixels with a spacing of 500  $\mu\text{m}$ . Both displays with "standard" OLEDs and transparent OLEDs were demonstrated. By applying the process and design improvements described above, we achieved displays with operating voltages below 10 V, operating currents of 10-20 microamperes ( $\mu\text{A}$ ), and series resistances of approximately 100 ohms ( $\Omega$ ). These displays are described in the publication, "See-through, multi-pixel organic emissive display," Electronics Letters, vol. 34, no. 9, 30 April 1998, pp. 915-916.

### **3.10.2 Second Phase Backplane Research**

During the second phase of the HDS contract (from 1998 to 2001), HRL served as a subcontractor to Princeton University. HRL's goal during this phase was the development of the



backplane technology for the realization of flexible active matrix OLEDs based on single crystal silicon-on-insulator (SOI) material system. The advantages of using this approach are: (1) The higher material quality of single crystal Si, compared to polycrystalline or amorphous Si, results in higher carrier mobilities, and hence, higher drive currents for the OLED pixels. Conversely, for a given drive current, active matrix OLEDs with higher pixel densities are realizable using this material system; (2) The higher carrier mobilities in single crystal Si can result in the monolithic integration of the high speed row and column drive electronic for the active matrix OLEDs; (3) The SOI technology allows a simpler device fabrication process compared to standard CMOS technology. Also, the lack of a conducting substrate in SOI will result in a much-reduced number of inter-pixel shorts, and hence, an improved active matrix OLED fabrication yield; (4) The insulating oxide layer of the SOI substrate serves as an ideal etch stop layer in our circuit transfer technique; (5) Our double transfer technique results in the transfer of any arbitrary circuit fabricated on a semiconductor wafer with an intermediate etch stop layer to another arbitrary substrate as a sheet layer. This allows the preservation of the original circuit geometry, for example the pixel pitch in our active matrix circuit, after the transfer process.

Our circuit transfer process involved the initial processing of the circuit on the active layer of bonded SOI wafers, after which the processed side of the wafer was bonded to a temporary support. This bonding was achieved using a layer of wax. After thinning the back Si substrate of the SOI wafer using chemo-mechanical polishing, the remainder of this substrate was completely removed in a KOH etching solution. The exposed oxide layer of the SOI wafer was then bonded to a permanent support, such as plastic or glass, using a layer of epoxy. Following the curing of the epoxy, the wax layer was removed in a solvent, thus releasing the permanent support bonded to the circuit with the sheet oxide layer in between. One of the key advantages of this technique is that the entire circuit is transferred as a *sheet* to another arbitrary substrate. This avoids transferring of the circuits in blocks or segments, as it is done in other circuit transfer techniques. Furthermore, the transfer of the circuit as a sheet layer maintains the original registration between individual sub-circuits, such as in an active matrix circuit array.

One of the key components in the realization of this transfer process was the development of a good adhesion layer between the photoresist-protected circuit and the temporary support wafer used. We found that spin-coating a suitable solution of Apiezon black wax in trichloroethylene (TCE) resulted in excellent adhesion between the two components mentioned above, without which our double transfer process could not be realized reliably.

Another important component in the development of this double-transfer process was the selection of a suitable epoxy for bonding the exposed oxide layer to a permanent support, as described above. This epoxy had to have two important properties: (1) a low expansion coefficient after curing in order not to impose a significant strain to the thin (1-2  $\mu\text{m}$ ) sheet oxide layer, and (2) be inert to TCE during the removal of the wax layer. After experimenting with a number of epoxy materials, we found a suitable epoxy for this transfer process (Tra-Bond F113 epoxy from TRA-CON). We used this epoxy for the permanent bonding of transferred circuits to both glass and mylar supports.

One of the key issues in the development of the SOI active matrix circuits for driving the OLED emitters was the formation of a good ohmic contact between the circuit metallization and the ITO anode of the OLED. We found that the combination of a thicker layer (5000 Å) of aluminum and a thinner (1000 Å) of TiW results in excellent ohmic contact formation. The aluminum layer formed a good ohmic contact to the p<sup>+</sup> source and drain regions of the PMOS transistors in the active matrix circuit. The TiW layer not only formed a good electrical contact to ITO, but also served to prevent the formation of an intermediate Al<sub>x</sub>O<sub>y</sub> current blocking layer during the ITO sputter deposition, which would have otherwise happened.

The two-transistor active matrix circuit fabricated on bonded SOI wafers had excellent characteristics. This was mainly due to the excellent electrical characteristics of the PMOS transistors used in these circuits. Due to the perfect single crystal silicon layer using which the PMOS transistors were fabricated, very high p-channel mobilities of more than 200 cm<sup>2</sup>/V-s were measured. Combined with low threshold voltages of less than 2 V, and very low leakage currents of less than 0.1 nA, these transistors resulted in active matrix circuits with excellent current holding capabilities. In fact, almost no drooping in the drain current of the PMOS transistor driving the organic LED display element was observed in a frame time of 16.7 ms (corresponding to a display frame rate of 60 Hz). This constant current maintaining in one frame time was obtained with storage capacitance values as low as 0.5 pF. The small value of the storage capacitance required, plus the small geometries of the two PMOS transistors in the active matrix circuit resulted in pixels with aperture ratios of more than 80% capable of providing more than 1 mA of drive current to the display element.

The successful fabrication of the active matrix circuit described above resulted in the successful demonstration of an active matrix OLED display. To the best of our knowledge, this display, which was based on a 64x64 array with a pixel pitch of 250 μm, was the first working active matrix OLED display based on SOI technology. We demonstrated that the OLED pixel luminance remained constant with almost no drooping in one display frame time of 16.7 ms. Ideally we would have liked to demonstrate an active matrix OLED display that was transferred to a plastic substrate. However, this was not accomplished mainly due to the lack of a good moisture and oxygen barrier layer or cover window with flexible characteristics at the time. This barrier layer is essential in the operation of the OLED. Nevertheless, we believe that we have demonstrated the two key elements towards the realization of a flexible active matrix OLED display. These two elements are the successful demonstrations of our novel double-transfer technique to plastic, and the active matrix OLED display, both based on the SOI technology. These flexible active matrix displays would be suitable for applications requiring display sizes smaller than 6-8 inches due to the limitations of the SOI wafer sizes.

Therefore, the main accomplishments of the HRL portion of the second phase of this program were two-fold: (1) the demonstration of a novel double transfer technique for the transfer of any arbitrary circuit fabricated on a semiconductor wafer with an intermediate etch stop layer to another arbitrary substrate, and (2) the demonstration of a monolithic two-transistor active matrix organic LED array using the silicon-on-insulator (SOI) technology with excellent active matrix circuit characteristics. We believe we have the first demonstration of an active matrix OLED display based on the SOI technology.

## 4. DISCUSSION

The objective of this program was to demonstrate both passive and active matrix, flexible, small scale displays based on small molecular weight organic light emitting device (OLED) technology. Our primary platform at the outset of the program in 1994 was a stacked, full color OLED, or SOLED based on fluorescent emission. It was our objective to integrate SOLEDs on flexible active matrix backplanes based on small arrays of Si on insulator transferred in thin film form from a Si wafer "handle". As the program progressed, several major developments resulted in our changing course from these initial directions to explore far more fertile areas of advance. Nevertheless, the initial directions proved successful on many fronts.

### 4.1 Demonstration of the First Transparent Organic Light Emitting Device (TOLED)

This device is a primary element needed in the SOLED structure. Its first realization consisted of overcoating a very thin Mg-Ag, semitransparent cathode with indium tin oxide (ITO) resulting in devices which were ~60% transparent. This device was further developed to completely eliminate the semitransparent metal film, replacing it with an organic "damage prevention layer." In this case, the so-called "metal-free TOLED", or MF-TOLED, was at least 80% transparent. Employing Li, n-type doping under the cathode also resulted in devices which were as or even more efficient than conventional, thick metal cathode based OLEDs. Today, TOLEDs are a key component, not only for SOLED technology, but also for AM displays where a transparent contact is needed for top emission. For example, the SONY 13-inch display employs transparent top contacts of the type used in the TOLED. Our team has secured all of the foundation patents regarding TOLED and MF-TOLED technology.

### 4.2 Demonstration of the First, Efficient, Full-Color Stacked OLED (SOLED)

Our initial version employed four contacts and standard TOLED sub pixel elements. We found that there were substantial microcavity effects distorting the output colors, and that the efficiency through the entire stack was reduced due to multiple, 60% transparent contacts separating the lower two sub-pixels. Also, central to the stack was an "inverted OLED", which had the cathode down and the anode up, opposite to the normal sense of the OLED. This device has a higher operation voltage than conventional OLEDs due to details of the cathode formation process. In spite of these shortcomings, the demonstration was a tour de force, a great success, showing the substantial promise of the concept. The SOLED then proved to be an ideal platform for pushing OLED technology and performance to its limits. To eliminate microcavity spectral distortion, we developed a theory for accurately modeling weak cavity effects in OLEDs, and then adjusted the structure to eliminate this parasitic property. In addition, we employed metal free TOLEDs to reduce absorption as light traversed the stack, thereby greatly improving the device efficiency. Finally, a separate and independent contact was made to the inner pixel to allow for separate ground connections to all three sub-pixel color elements. This eliminated the need for differential biasing of the sub-pixels to create the desired color and intensity emission from the pixel. Other work regarding SOLED technology included developing means for pixel driving and addressing, and for pixel deposition using moveable shadow masks. While it ultimately proved that the SOLED platform was too difficult to manufacture given the current state of the art in small

molecular weight materials and devices, it is apparent that this technology has numerous advantages over the current technology of side by side positioning such as improved fill factor, higher fidelity color rendering, and higher resolution display capabilities. Hence, we believe that as the manufacturing technology matures, SOLEDs will be developed to meet advanced display needs. In the mean time, the stacking concept has been used in full color back lights and other applications where different TOLED color pixels are fabricated on independent substrates, and then stacked into a single, full color generating “sandwich”. Considerable foundation IP and a strong patent position was obtained by our team for the practice of SOLED technology.

### **4.3 Flexible Organic Light Emitting Diode (FOLED)**

An additional key technology pursued in our early efforts was the flexible OLED, or FOLED. The flexible back plane was needed for both AM and PM applications. Reports in the literature suggested that only polymers would be adaptable to truly flexible electronics such as displays due to their comparatively robust mechanical properties. Our principle concern with generating FOLEDs based on small molecular weight materials centered on defects known to exist on rough ITO substrates punching holes in the very thin molecular materials. Also, there were concerns regarding the brittleness of ITO. We found suitable flexible substrates with smooth ITO, thereby enabling the demonstration of the first small molecule based FOLED technology. The substrates used consisted of PET, which is not an adequate moisture barrier to protect the OLEDs from long term environmental degradation. This issue has since been explored by several labs worldwide, most particularly by our team member, Universal Display Corp. Moisture barrier substrates today are currently allowing for FOLED-based displays with >5000 hr operational lifetimes. Concurrent to this development, we began our work with flexible, crystalline Si AM backplanes with our team member, HRL, Inc. Early work with this process of separating the transistors from the substrate after deposition of a silicon dioxide base resulted in the demonstration of an integrated OLED with a flexible Si transistor backplane. While this proof of concept device was useful in exercising the integration technology, it became clear that its major application would be restricted to microdisplays, where flexibility is not of the primary concern. Hence, in 2000, we abandoned further exploration of the flexible Si backplane transfer technology. This work resulted in foundation patent protection of small molecule based flexible display applications for our team.

### **4.4 Organic Vapor Phase Deposition (OVPD) of OLEDs**

In the realm of manufacturing, we demonstrated that the new technology of organic vapor phase deposition (OVPD) first demonstrated by our team for use in the growth of nonlinear optical organic crystals, could also be adapted to the growth of OLEDs for large area displays. Hence, we demonstrated the growth of OLEDs employing this efficient manufacturing process with performance comparable to that of devices grown by vacuum deposition. In addition, we demonstrated that OVPD could be applied to the growth of optically pumped laser structures. A major innovation in OVPD growth under this program was the growth at reduced pressures – typically ~0.1-1 Torr – to obtain high density, high quality films. A multibarrel reactor was built for the deposition of heterostructures consisting of several layers, some of them doped to achieve high luminescence. Extending further our work on OVPD, we modified the horizontal, hot

walled growth reactor to accommodate the translation through the growth zone of extended flexible substrates. In this experiment, we demonstrated the uniform and controlled growth of doped and undoped OLED heterostructures over a substrate 30 cm in length by 7 cm wide, suggesting the applicability of OVPD to large scale, web processing of OLEDs. The single most significant accomplishment of this OVPD research was the development of analytical models predicting the growth modes and properties as a function of reactor conditions. Extending these models, we were able to predict the appropriate mask geometry and deposition conditions leading to very high precision patterned deposition of OLED pixels and other organic electronic structures. We have been able to demonstrate, based on conditions predicted in our models, the deposition of pixels with 6 micron diameters, and pattern resolutions approaching 1 micron. During this program, our team also began work with Aixtron, AG, the largest supplier of MOCVD equipment worldwide. Aixtron, in partnership with Universal Display Corp. and Princeton University, is in the process of building both research and manufacturing OVPD tools for the display industry. OVPD has also proven its utility in the growth of high mobility pentacene organic thin film transistors. For example, we demonstrated that OVPD could be used under a variety of growth conditions to control the crystallite size of the organic in the channel of the transistor. Under appropriate, near equilibrium growth conditions, we obtained field effect mobilities of  $1.4 \text{ cm}^2/\text{V-s}$  with crystals extending across the entire several micron long gate region from source to drain. Such thin film transistors are of interest for fully organic display back planes, and their demonstration was a further objective of our program. A foundation patent position in OVPD has been developed by our team under the support of this program.

#### **4.5 Electrophosphorescent Organic Light Emitting Diode (PHOLED)**

The largest breakthrough of the program came in 1998, when our team successfully demonstrated that triplet *and* singlet excitons could be harvested for light emission using heavy metal organic compounds based on Pt or Ir complexes. This process, known as phosphorescence, provides the opportunity for obtaining 100% internal quantum efficiency in OLEDs – a factor of four higher than that obtainable through the conventional mechanism of singlet emission through fluorescence. The chemical suite developed by our team has allowed us to span the color gamut, from the red through the deep blues, employing triplet emitting materials of extremely high efficiencies. For example, we have demonstrated 19% *external* efficiency in the green, 14% in the red and orange, and 6% in the light blue spectral regions. This finding has made a significant difference in the prospect of OLEDs for display applications – currently every major OLED manufacturing team world wide is pursuing phosphor emission and many have reproduced our results in achieving very high efficiencies. Soon after the demonstration of electrophosphorescence, we demonstrated that phosphor molecules could be co-doped with fluorophores as a “sensitizer”, allowing fluorescent devices to also harvest both singlets and triplets from the host conductive organic matrix. This too, has resulted in significant improvements in fluorescent devices. Our team demonstrated 8% external efficiency sensitized OLED for a red dye, DCM2, whose fluorescence efficiency when used in an OLED is typically <1%. In further work, we identified and quantified the observed fall off in phosphorescent quantum efficiency at high luminances as being due to triplet-triplet annihilation. By decreasing the radiative phosphorescent lifetime of the molecules, we found that such efficiency roll-offs could be substantially reduced. The strong metal-ligand-charge-transfer triplet state of the Ir

organometallics is particularly advantageous in this regard, leading to triplet lifetimes of only a few hundred nanoseconds when used in conductive hosts such as carbazol biphenyl (CBP). Indeed, using such guest-host combinations in electrophosphorescent OLEDs (PHOLEDs), exceeding those of fluorescent OLEDs have been achieved at very high integrated quantum efficiencies. To fully exploit the high efficiencies inherent in PHOLEDs, we introduced the exciton/hole blocking layer concept which "bottles up" the excitation in the emission zone, thereby preventing exciton quenching and its concomitant loss in PHOLED efficiency at contacts or in transporting layers. Using this device architecture, companies such as Samsung in Korea have demonstrated full color, PHOLED displays of unprecedented high efficiencies. Finally, we have demonstrated that the operational lifetime of PHOLEDs can well exceed that obtained via fluorescence, extending in some cases to  $>10^6$  hrs (extrapolated). More typically, 20,000 to 50,000 hrs lifetimes (extrapolated) in the red and the green have been demonstrated under conventional display operating conditions. Our team has developed a significant and foundational patent position in all aspects of electrophosphorescence and phosphor materials.

#### **4.6 Additional Technologies Invented and Fundamental Advances**

Several other technologies were introduced in our program, as well as some fundamental advances. These are briefly listed here.

We developed a model to understand carrier transport in organic thin film devices based on trap limited space charge conduction. This model is helpful in determining the current vs. voltage as well as the thermal dependence of OLEDs. Next, we extended this model into the microscopic domain, and find that the current in thin amorphous films is ultimately limited by traps at the dipolar layer at the organic/electrode interface.

We discovered the solid state solvation effect, whereby the color emission from fluorescent and phosphorescent dopants can be shifted substantially across the visible spectrum simply by varying their concentrations in a dipolar molecular host. This effect is useful for color tuning OLEDs across a wide spectral range using only a single dopant species.

We demonstrated that microlens arrays, as well as shaped substrates, can effectively increase the light outcoupling efficiency from glass substrates used in OLEDs without destroying the image quality of the displays. In particular, microlens arrays can be fabricated extremely inexpensively employing elastomers poured into hemispherical molds. Then the elastomeric lens array is simply attached to the substrate surface, increasing the outcoupling efficiency by a factor of 1.5 to 2.

Several different pixel patterning technologies were explored. Perhaps the most promising is cathode patterning via stamping, whereby a continuous cathode layer is deposited uniformly across the organic heterostructure surface. Then a stamp embossed in the desired electrode pattern is coated with the same electrode metal, and is pressed against the unpatterned metal/organic surface. By employing an adequately high pressure, the metal on the stamp cold-welds to that on the organic. Further pressure causes the metal at the edges of the stamp to fracture, and then removing the stamp carries away the metal from the organic layers in the areas

under pressure, leaving behind the desired electrode pattern. A converse, metal additive process which works at considerably lower pressures was also demonstrated. In that process, the source-drain contacts of pentacene channel organic thin film transistors were demonstrated. In the additive process, a very thin metallic "strike" layer is first deposited onto the organic surface. A thicker metal is then deposited onto the stamp, whose surface is precoated with an adhesion reduction layer. The stamp is brought into contact with the strike layer surface, cold welding ensues, and the thick metal on the stamp is then left behind on the strike layer as the stamp is parted from the substrate. Finally, the residual strike layer metal between the thick metal left from the stamp is removed from the organic surface by a light dry etch step.

## 5. CONCLUSIONS

This eight-year effort has resulted in many fundamental advances in the state of the art in OLED technology, and in some cases has set the agenda and standard for current and future research on OLEDs world wide. The technologies with the most profound impact are the demonstration of electrophosphorescence, top emission, and organic vapor phase deposition. Without these demonstrations, much if not all of the promise of OLEDs today would not be apparent, and it is conceivable that OLED technology would not be considered to be the strong contender for the next generation of high information content displays that it currently is.

On top of these advances, the demonstration that small molecular weight OLEDs can be as flexible as polymer based OLEDs combines all of the advantages of small molecules such as ultrahigh efficiency and ease of patterned deposition, with the processability of polymers. We can now look forward to a completely new generation of highly capable OLED displays that are several times more efficient than LCDs, with also having the attributes of flexibility and transparency.

Finally, the demonstration of stacked full color pixels (SOLEDs) was a major accomplishment on several fronts. It has opened the door to high resolution head-mounted and table-mounted displays, and at the same time its demonstration required the solution and understanding of many fundamental problems then confronting OLED displays. It is fair to credit the demonstration of the SOLED platform with the invention of the transparent OLED, patterning of organics via *in situ* shadow mask translation and stamping, as well as electrophosphorescence. In addition, our work in SOLEDs also resulted in fundamental understandings of weak microcavity effects in all OLEDs, as well as color shifting via the solid state solvation effect and the understanding of basic carrier transport properties in organic thin film devices. Hence, while SOLEDs presented a device architecture which has important applications in its own right, it also has provided an ideal laboratory for investigating the fundamental aspects of electroluminescence in organics.

This program has also resulted in a strong collaboration between USC, Princeton University and UDC that has worldwide recognition. Indeed, DARPA funds and AFRL management has played an important role in the successful launch of UDC, a major player in OLED display technology in the US as well as globally.



## **6. RECOMMENDATIONS**

While enormous ground in OLED research and development has been covered under the auspices of this grant, and indeed by the entire technical community during the duration of this work, still much is left to be done if we are to realize the full potential of this strategically important device concept. Five major issues and challenges should be addressed in future work as described below.

### **6.1 GLASS SUBSTRATE PRODUCTS**

The operational lifetime of OLEDs on-glass requires further improvements. This is particularly true of the blue phosphor and fluorescent family of dopants. Blue emission presents special challenges of both a fundamental and practical nature, which have yet to be fully understood. This remains a most fruitful area of research.

### **6.2 MANUFACTURING TECHNOLOGY**

Low cost patterning and deposition of organic thin films over large substrate areas, and on flexible substrates has yet to be convincingly demonstrated. OLED technology is arguably the most powerful paradigm shift in display technology since the invention of the LCD. However, to displace LCDs, OLEDs must be capable of manufacture at very low cost and at high throughput and yields. Here, organic vapor phase deposition and patterning by stamping are two technologies of particular promise for the solution of these problems.

### **6.3 FLEXIBLE SUBSTRATE TECHNOLOGY**

Flexible, long operational lifetime displays fully integrated with advanced electronics promises to usher in a new generation of communication devices that are lightweight, compact, and highly portable. Yet, operational lifetime and fabrication issues that are still unsolved for OLEDs deposited on glass substrates are even more difficult to address for flexible displays on plastic substrates. However, the advantages brought by such integrated flexible displays make the challenges highly worthwhile to address and to solve.

### **6.4 TRANSPARENT DISPLAY TECHNOLOGY**

A new range of display applications and architectures are also made possible using transparent OLEDs and contacts also developed in this program. However, their operational lifetimes and manufacturing yields still need considerable improvement to be practical. Furthermore, investigations based on understanding the modes of current injection, and the limitations introduced by semi-transparent and metal-free cathodes need to be supported. There is considerable benefit to do this, not the least of which is to develop electrical contacts suitable for organic thin film lasers and high efficiency solid state lighting fixtures.

### **6.5 MATERIALS FOR OLED STRUCTURES**

There is little question that all of the materials used in OLEDs to date, and in other organic electronic devices, are far from optimal in their properties. Hence, a vigorous research effort needs to be mounted to optimize phosphors, ETLs, HTLs, blocking layers as well as electrode and carrier injection layers. The pay-off for materials improvement is enormous and needs constant attention to ensure continual progress.

## 7. SYMBOLS, ABBREVIATIONS, AND ACRONYMS

AFRL	Air Force Research Laboratory (in Dayton OH)
Alq <sub>3</sub>	Tris(8-hydroxyquinolinato) aluminum, aka aluminum trisquinolate, (electron transporting layer material; also, the emissive layer in original OLEDs)
AM	Active matrix (active element holds desired electrical signal for full frame time), (backplane substrate TFT array used to address AMOLED), (see passive matrix)
AMOLED	Active matrix organic light emitting display
Backplane	Electrical circuitry built on back substrate of a flat panel display to apply electrical representation of an image in a manner (driver-conditioned signals) that modulates/controls photonic emission from each picture element.
BAIq	Aluminum(III)bis(2-methyl-8-quinolinato)4-phenylphenolate, (hole blocking layer material)
BCP	2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (hole blocking layer material)
Brightness	Psychological dimension in which visual stimuli are ordered continuously from light to dark and which is correlated with light intensity
btIr	A red phosphor based on Iridium
btP Ir	A red phosphor based on Iridium
ca.	Calculated
CBP	N,N'-dicarbazolyl-4,4'-biphenyl (host material for emissive layer of device)
Candella	Luminous intensity of a source emitting 540 GHz radiation at an intensity of $683^{-1} \text{ w sr}^{-1}$ in a given direction.
Cd	Candella
cd/m <sup>2</sup>	Candella per square meter (standard unit of luminous intensity per unit area)
cd/A	Candella per Ampere (unit for measuring of luminance efficiency) (unit of energy conversion efficiency in current driven device)
CIE	Commission Internationale de l'Éclairage (standard color space coordinates)
cm <sup>2</sup> /V-s	Unit of charge mobility (in semiconductor materials subjected to electric field)
CMOS	Complementary metal oxide semiconductor (power-conserving circuit design)
Cp <sup>5φ</sup> •	1,2,3,4,5-pentaphenylcyclopentadienyl radical
CRE	Color rendering index
CuPc	Copper phthalocyanine (hole injection layer material)
C <sup>-</sup> N	mono-anionic cyclometallating ligand
DARPA	Defense Advanced Research Projects Agency
DCM2	Red dye (a fluorescent material)
EBL	Electron blocking layer
EL	Electroluminescent
Electroluminescence	Luminescence resulting from application of electrical energy to a material
Electrophosphorescence	Luminescence caused by application of electrical power (current) via energy excited states similar to, or identical with, those involved in phosphorescence
EPR	Electron paramagnetic resonance.
ET	Electron transporter (layer within a device structure)
ETM	Electron transporter material

Fluorescence	Radiation emitted (usu. visible) resulting from and occurring only during the absorption of radiation (e.g. ultraviolet or two-photon infrared) from some other source. The absorbed radiation (e.g. UV) is often the result of an electrical discharge, with two energy conversions occur (from electrical to optical UV to visible).
Fluorescent	Glowing as a result of fluorescence
FOLED	Flexible OLED
HBL	Hole blocking layer
HDS	High Definition Systems (applied research program for displays at DARPA)
HOMO	Highest occupied molecular orbital
HRL	Hughes Research Lab (in Malibu CA)
HT	Hole transporter (layer within a device structure)
HTM	Hole transporter material
Inverted OLED	Device with cathode "down" and the anode "up" (opposite to the normal sense of an OLED structure). The direction for observation of emitted light is often through the top (anode) surface.
IP	Intellectual property
Ir	Iridium (atomic element)
Ir complexes	Heavy metal complex dopant, or phosphor, based on Ir
Ir(ppy) <sub>3</sub>	Iridium tris-(phenyl-pyridine). (Also sometimes written Irppy)
ISB	<i>bis</i> -iminostilbene-biphenyl
ISF	N,N'-iminostilbene-4,4'-fluorene
ITO	Indium tin oxide (material for fabrication of transparent, thin-film electrodes)
KOH	Potassium hydroxide (etching solution used in thin-film electronics fabrication)
L <sub>0</sub>	Initial luminance (value at t = 0 for a newly made display device)
LE	Luminous efficiency (in cd/A)
lm	Lumen
lm/W	Lumen per Watt (power conversion efficiency unit for electro-optical device)
Lumen	Unit of luminous flux equal to the light emitted in a unit solid angle by a uniform point source of one candella intensity.
luminance	Luminous intensity of a surface in a given direction per unit of projected area
luminescence	Quality or state of emitting or reflecting usu. steady, suffused, or glowing light
lumophore	luminescent molecule
LX	ancillary bidentate (ligand)
LUMO	Lowest unoccupied molecular orbital
mCP	N,N'-dicarbazolyl-3,5-benzene (a material doped to create a luminescent layer)
MLCT	Metal-ligand charge transfer
MF-TOLED	Metal-free TOLED
MOCVD	Metal oxide chemical vapor deposition
niBr	N-2,6 dibromophenyl-1,8-naphthalimide (electron transporter film material)
NPD	N,N'-diphenyl-N,N'dinaphthylbenzidine (hole transporting material)
OLED	Organic light emitting diode (device, display)
OVPD	Organic vapor phase deposition
O <sup>^</sup> O	diketonate ligand
PH-OLED	Phosphorescent OLED

Phosphorescence	Luminance that is caused by the absorption of radiations and continues for a noticeable time after these radiations have stopped; an enduring luminescence without sensible heat. Emission is from an excited state with forbidden direct transition to ground state (i.e. low probability direct optical transitions), (e.g. triplet excited state emissions in most materials).
Phosphorescent	Light emitted involving non-optically allowed transitions
Pixel	Picture element, smallest portion of a display device capably of producing the full range of colors, graylevels, and angular distribution function of the full display
PM	Passive matrix (multiplexed electrical addressing scheme involving the sequential application of signals to each pixel of the display device; no active element exists in the display screen to retain the image control signals during frame time), (perception of a complete image relies on the relatively slow chemistry in the retina of the human eye to create an illusion that the entire image is present), (OLED light emission occurs only at moment control signal is applied to pixel). is present), (requires higher peak power or current at each pixel).
PMOS	Positively-doped-channel metal oxide semiconductor
POEM	Center for Photonics and Optoelectronic Materials (at Princeton University)
ppy	Phenyl pyradine (a ligand molecule used in forming dopants, aka phosphors)
Pt	Platinum (atomic element)
Pt complex	Heavy metal complex dopant, or phosphor, based on cyclometalated Pt
PU	Princeton University (in Princeton NJ)
Sheet Resistance	Ratio of material resistivity to sheet thickness (in $\Omega/\square$ )
Si	Silicon (atomic element)
SOI	Silicon on insulator
SOLED	Stacked OLED
$T_{1/2}$	Half-life (in hrs)
$T_g$	Glass transition temperature
TiN	Titanium nitride
TiW	Titanium tungsten
TFT	Thin film transistor
TOLED	Transparent OLED
Torr	Unit of pressure
TCE	Trichloroethylene
TPD	N,N-di-(3-methylphenyl)-N,N diphenyl-4,4-diaminobiphenyl
UDC	Universal Display Corporation (in Ewing NJ)
USC	University of Southern California (in Los Angeles CA)
UV	Ultraviolet
WOLED	White OLED
$\alpha$ -NPD	4,4'-bis[N-(1-naphthyl)-N-phenylamino]biphenyl (an HTL material)
$\phi$	$C_6H_5$ (phenyl unit)
$\eta_{ext}$	External quantum efficiency
$\lambda_{max}$	Wavelength at which maximum light emission is observed
$\Omega$	Ohm
$\square$	Ratio of the length to the width of a thin film conductor
$\Omega/\square$	Unit of sheet resistance; resistance per unit area of a thin-film electrical contact

**APPENDIX A.**  
**LIST OF PATENTS RESULTING FROM THIS DARPA-SPONSORED GRANT**

1. Mixed Vapor Deposited Films For Electroluminescent Devices, Inventor(s): S. Forrest (Princeton, NJ), M. Thompson (Los Angeles, CA), P. Burrows (Richland, WA), D. McCarty, L. Sapochak (Las Vegas, NV), J. Cronin, Assignee: Princeton University, Application No. 08/693,359, US Patent 6358631.
2. Fluorescent Dye Dopants Based on Jelly Fish Chromophore, Inventor(s): M. Thompson (Los Angeles, CA), Y. You, N. Petasis, Assignee: Princeton University, Application No. 08/948,130, US Patent 6030715
3. Method of Making Transparent Contacts to Organic EL Devices and Other Organic Devices, Inventor(s): S. Forrest (Princeton, NJ), P. Burrows (Richland, WA), V. Bulovic (Cambridge, MA), G. Gu, M. Thompson (Los Angeles, CA), Assignee: Princeton University, Application No. 08/613,207, US Patent 5703436
4. Method of Making Transparent Contacts to Organic EL Devices and Other Organic Devices, Inventor(s): S. Forrest (Princeton, NJ), P. Burrows (Richland, WA), V. Bulovic (Cambridge, MA), G. Gu, M. Thompson (Los Angeles, CA), Assignee: Princeton University, Application No. 08/872,560, US Patent 6264805
5. Ink Jet Printed Display, Inventor(s): S. Forrest (Princeton, NJ), M. Thompson (Los Angeles, CA), Assignee: Princeton University, Application No. 08/772,333, US Patent 6013982
6. Stacked Display of Transparent OLED, Inventor(s): S. Forrest (Princeton, NJ), P. Burrows (Richland, WA), D. Garbuzov (Cranbury, NJ), Assignee: Princeton University, Application No. 08/925,403, US Patent 5874803
7. 3-Color Display with Phosphor Downconvertors, Inventor(s): S. Forrest (Princeton, NJ), P. Burrows (Richland, WA), D. Garbuzov (Cranbury, NJ), Assignee: Princeton University, Application No. 08/794,595, US Patent 6091195
8. PTCDA and Analogous Compounds as Hole Injection Enhancers in OLED, Inventor(s): S. Forrest (Princeton, NJ), M. Thompson (Los Angeles, CA), P. Burrows (Richland, WA), V. Bulovic (Cambridge, MA), Assignee: Princeton University, Application No. 08/865,491, US Patent 5998803
9. Method for Deposition and Patterning of Organic Thin Film, Inventor(s): S. Forrest (Princeton, NJ), V. Bulovic (Cambridge, MA), P. Burrows (Richland, WA), Assignee: Princeton University, Application No. 08/976,666, US Patent 5953587
10. Stacked OLEDs for High Brightness Light Source, Inventor(s): P. Burrows & S. Forrest (Princeton, NJ), Assignee: Princeton University, Application No. 09/192,316, US Patent 6274980
11. Thermally Stable (Iminostilbene and Iminodibenzyl) Hole Transporters, Inventor(s): M. Thompson (Los Angeles, CA), D. Loy, B. Koene, D. O'Brien, S. Forrest (Princeton, NJ), Assignee: Princeton University, Application No. 09/610,454, US Patent 6333521

12. Bright Red-Emitting Organic LEDs (OLEDs), Inventor(s): S. Forrest (Princeton, NJ), P. Burrows (Richland, WA), M. Thompson (Los Angeles, CA), Assignee: Princeton University, Application No. 08/774,087, US Patent 6048630
13. High Contrast Transparent Organic Light Emitting Device Display, Inventor(s): S. Forrest (Princeton, NJ), P. Burrows (Richland, WA), M. Thompson (Los Angeles, CA), Assignee: Princeton University, Application No. 08/821,380, US Patent 5986401
14. Method of Fabricating and Patterning OLEDs, Inventor(s): S. Forrest (Princeton, NJ), P. Burrows (Richland, WA), P. Tian, Assignee: Princeton University, Application No. 08/977,205, US Patent 6013538
15. Improved Method for Growth of Indium Tin Oxide Electrode INTOLEDs, Inventor(s): S. Forrest (Princeton, NJ), P. Burrows (Richland, WA), Z. Shen (Princeton, NJ), Assignee: Princeton University, Application No. 08/928,800, US Patent 5981306
16. Improved 3-Color Stacked Organic Light Emitting Device, Inventor(s): S. Forrest (Princeton, NJ), P. Burrows (Richland, WA), Assignee: Princeton University, Application No. 08/792,046, US Patent 5917280
17. Method of Achieving Bias on Stacked OLED, Inventor(s): S. Forrest (Princeton, NJ), P. Burrows (Richland, WA), Assignee: Princeton University, Application No. 08/792,050, US Patent 5757139
18. Bright Red-Emitting Organic LEDs (OLEDs), Inventor(s): S. Forrest (Princeton, NJ), P. Burrows (Richland, WA), M. Thompson (Los Angeles, CA), Assignee: Princeton University, Application No. 09/358,086, US Patent 6329085
19. Display Driving Method and Device, Inventor(s): S. Forrest (Princeton, NJ), M. Thompson (Los Angeles, CA), Assignee: Princeton University, Application No. 09/493,099, US Patent 6366268
20. Color-Tunable Organic Light Emitting Devices, Inventor(s): M. Thompson (Los Angeles, CA), V. Bulovic (Cambridge, MA), S. Forrest (Princeton, NJ), Assignee: Princeton University, Application No. 09/207,799, US Patent 6312836
21. Method for Deposition and Patterning of Organic Thin Film, Inventor(s): S. Forrest (Princeton, NJ), V. Bulovic (Cambridge, MA), Assignee: Princeton University, Application No. 09/344,722, US Patent 6297516
22. Highly Transparent Non-Metallic Cathodes, Inventor(s): S. Forrest (Princeton, NJ), P. Burrows (Richland, WA), G. Parthasarathy, D. O'Brien, Assignee: Princeton University, Application No. 09/054,707, US Patent 6420031
23. Structure for High Efficiency Electroluminescent Device, Inventor(s): M. Baldo, D. O'Brien, S. Forrest (Princeton, NJ), Assignee: Princeton University, Application No. 09/153,144, US Patent 6097147
24. Metal 8-hydroxy-quinoxaline Materials as Hosts for Red Organic Light Emitting Diodes, Inventor(s): P. Burrows (Richland, WA), S. Forrest (Princeton, NJ), M. Thompson (Los Angeles, CA), A. Shoutikov, Y. You, Assignee: Princeton University, Application No. 08/838,099, US Patent 5861219

25. A Method for Color-Tuning the Emission of OLEDs, Inventor(s): V.Bulovic (Cambridge, MA), S. Forrest (Princeton, NJ), M. Thompson (Los Angeles, CA), Assignee: Princeton University, US Patent 6287712
26. High Efficiency Organic Light Emitting Devices with Light Directing Structures, Inventor(s): S. Forrest (Princeton, NJ), P. Burrows (Richland, WA), V.Bulovic (Cambridge, MA), D.Garbuzov (Cranbury, NJ), Assignee: Princeton University, Application No. 08/772,332 US Patent 5834893
27. Method for Making High Reliability, High Efficiency, Integratable OLEDs , Inventor(s): S. Forrest (Princeton, NJ), P. Burrows (Richland, WA), V.Bulovic (Cambridge, MA), D.Garbuzov (Cranbury, NJ), Assignee: Princeton University, Application No. 08/774,119, US Patent 6046543
28. Multicolor organic light emitting devices, Inventors: Forrest; Stephen Ross (Princeton, NJ); Thompson; Mark Edward (Hamilton Square, NJ); Burrows; Paul Edward (Princeton, NJ); Sapochak; Linda Susan (Florham Park, NJ); McCarty; Dennis Matthew (Southampton, NJ), Assignee: Princeton University, US Patent 5707745
29. Multicolor organic light emitting devices, Inventors: Forrest; Stephen Ross (Princeton, NJ); Thompson; Mark Edward (Hamilton Square, NJ); Burrows; Paul Edward (Princeton, NJ); Sapochak; Linda Susan (Florham Park, NJ); McCarty; Dennis Matthew (Southampton, NJ), Assignee: Princeton University, US Patent 5721160
30. Multicolor organic light emitting devices, Inventors: Forrest; Stephen Ross (Princeton, NJ); Thompson; Mark Edward (Hamilton Square, NJ); Burrows; Paul Edward (Princeton, NJ); Sapochak; Linda Susan (Florham Park, NJ); McCarty; Dennis Matthew (Southampton, NJ), Assignee: Princeton University, US Patent 5757026
31. Vacuum deposited, non-polymeric flexible organic light emitting devices, Inventors: Gu; Gong (Princeton, NJ); Burrows; Paul (Princeton, NJ); Forrest; Stephen R. (Princeton, NJ), Assignee: Princeton University, US Patent 5844363
32. Saturated full color stacked organic light emitting devices, Inventors: Shen; Zilan (Lawrenceville, NJ); Forrest; Stephen R. (Princeton, NJ); Burrows; Paul (Princeton, NJ), Assignee: Princeton University, US Patent 5932895
33. Method and apparatus for measuring film spectral properties, Inventor(s): Forrest; Stephen R. (Princeton, NJ); Burrows; Paul E. (Princeton, NJ); Garbuzov; Dmitri Z. (Princeton, NJ); Bulovic; Vladimir (Metuchen, NJ), Assignee: Princeton University, US Patent 6005252
34. Organic light emitting devices, Forrest; Stephen Ross (Princeton, NJ); Thompson; Mark Edward (Hamilton Square, NJ); Burrows; Paul Edward (Princeton, NJ); Sapochak; Linda Susan (Florham Park, NJ); McCarty; Dennis Matthew (Southampton, NJ), Assignee: Princeton University, US Patent 6030700
35. Organic semiconductor laser, Inventors: Kozlov; Vladimir (Plainsboro, NJ); Forrest; Stephen R. (Princeton, NJ); Burrows; Paul (Princeton, NJ); Bulovic; Vladimir (Metuchen, NJ), Assignee: Princeton University, US Patent 6045930

36. Organic semiconductor laser, Inventors: Kozlov; Vladimir (Plainsboro, NJ); Forrest; Stephen R. (Princeton, NJ); Burrows; Paul (Princeton, NJ); Bulovic; Vladimir (Metuchen, NJ), Assignee: Princeton University, US Patent 6111902
37. Light emitting devices having high brightness, Inventors: Forrest; Stephen R. (Princeton, NJ); Burrows; Paul (Princeton, NJ); Garbuzov; Dimitri Z. (Princeton, NJ), Assignee: Princeton University, US Patent 6125226
38. OLEDs containing thermally stable glassy organic hole transporting materials, Inventors: Thompson; Mark E. (Anaheim, CA); Douglas; Loy (Lakewood, CA); O'Brien; Diarmuid (Princeton, NJ); Koene; Bryan E. (South Pasadena, CA); Forrest; Stephen R. (Princeton, NJ), Assignee: Princeton University, US Patent 6150043
39. Organic vertical-cavity surface-emitting laser, Inventors: Kozlov; Vladimir (Plainsboro, NJ); Forrest; Stephen R. (Princeton, NJ); Burrows; Paul (Princeton, NJ); Bulovic; Vladimir (Metuchen, NJ), Assignee: Princeton University, US Patent 6160828
40. Light emitting device using dual light emitting stacks to achieve full-color emission, Inventors: Thompson; Mark (Anaheim, CA); Forrest; Stephen R. (Princeton, NJ); Gu; Gong (Princeton, NJ), Assignee: Princeton University, US Patent 6166489
41. Stacked organic photosensitive optoelectronic devices with a mixed electrical configuration, Inventor(s): Forrest; Stephen R. (Princeton, NJ); Bulovic; Vladimir (Metuchen, NJ), Assignee: Princeton University, US Patent 6198091
42. Stacked organic photosensitive optoelectronic devices with an electrically parallel configuration, Inventors: Bulovic; Vladimir (Metuchen, NJ); Forrest; Stephen R. (Princeton, NJ), Assignee: Princeton University, US Patent 6198092
43. Color-tunable organic light emitting devices, Inventors: Thompson; Mark (Anaheim, CA); Bulovic; Vladimir (Metuchen, NJ); Forrest; Stephen R. (Princeton, NJ); Shoustikov; Andrei (Los Angeles, CA), Assignee: Princeton University, US Patent 6210814
44. Method for patterning light emitting devices incorporating a movable mask, Inventors: Burrows; Paul E. (Princeton Junction, NJ); Forrest; Stephen R. (Princeton, NJ); Bulovic; Vladimir (Metuchen, NJ); Tian; Peifang (Princeton, NJ); Brown; Julie (Princeton, NJ), Assignee: Princeton University, US Patent 6214631
45. Saturated full color stacked organic light emitting devices, Inventors: Shen; Zilan (Lawrenceville, NJ); Forrest; Stephen R. (Princeton, NJ); Burrows; Paul (Princeton, NJ), Assignee: Princeton University, US Patent 6232714
46. Stacked organic photosensitive optoelectronic devices with an electrically series configuration, Inventors: Forrest; Stephen R. (Princeton, NJ); Bulovic; Vladimir (Metuchen, NJ), Assignee: Princeton University, US Patent 6278055
47. Method of making a display, Inventors: Thompson; Mark E. (Anaheim Hills, CA); Forrest; Stephen R. (Princeton, NJ), Assignee: Princeton University, US Patent 6,245,393
48. OLEDs doped with phosphorescent compounds, Inventor(s): Thompson; Mark E. (Anaheim, CA); You; Yujian (Los Angeles, CA); Shoustikov; Andrei (Los Angeles, CA); Sibley; Scott



- (Baltimore, MD); Burrows; Paul E. (Princeton Junction, NJ); Forrest; Stephen R. (Princeton, NJ), Assignee: Princeton University, US Patent 6303238
49. Organic semiconductor lasers, Inventor(s): Burrows; Paul E. (Princeton Junction, NJ); Forrest; Stephen R. (Princeton, NJ); Thompson; Mark (Anaheim, CA); Kozlov; Vladimir G. (Plainsboro, NJ); Parthasarathy; Gautam (Princeton, NJ) Assignee: Princeton University, US Patent 6330262
  50. Phosphorescence Sensitized OLED, Inventor(s): S. Forrest (Princeton, NJ), M. Thompson (Los Angeles, CA), M. Baldo, Assignee: Princeton University, Application No. 09/915,130, US Patent 6310360
  51. Organic light emitting devices, Inventor(s): Forrest; Stephen Ross (Princeton, NJ); Thompson; Mark Edward (Hamilton Square, NJ); Burrows; Paul Edward (Princeton, NJ); Sapochak; Linda Susan (Florham Park, NJ); McCarty; Dennis Matthew (Southampton, NJ), Assignee: Princeton University, US Patent 6,365,270
  52. Organic semiconductor laser, Inventor(s): Kozlov; Vladimir (Plainsboro, NJ); Forrest; Stephen R. (Princeton, NJ); Burrows; Paul (Princeton, NJ); Bulovic; Vladimir (Metuchen, NJ), Assignee: Princeton University, US Patent 6,396,860
  53. Color-tunable organic light emitting devices, Inventors: Bulovic; Vladimir (Metuchen, NJ); Forrest; Stephen R. (Princeton, NJ); Thompson; Mark E. (Anaheim, CA), Assignee: Princeton University, US Patent 6287712
  54. Method for patterning devices, Inventor(s): Kim; Changsoon (Princeton, NJ); Burrows; Paul E. (Princeton Junction, NJ); Forrest; Stephen R. (Princeton, NJ), Assignee: Princeton University, US Patent 6294398
  55. Low pressure vapor phase deposition of organic thin films, Inventors: Forrest; Stephen R. (Princeton, NJ); Burrows; Paul E. (Princeton Junction, NJ); Ban; Vladimir S. (Princeton, NJ), Assignee: Princeton University, US Patent 6337102
  56. OLEDs containing thermally stable glassy organic hole transporting materials, Inventors: Thompson; Mark E. (Anaheim, CA); Douglas; Loy (Lakewood, CA); Forrest; Stephen R. (Princeton, NJ); Koene; Bryan E. (Watertown, MA); O'Brien; Diarmuid (Princeton, NJ), Assignee: Princeton University, US Patent 6387544
  57. Method for patterning devices, Inventors: Burrows; Paul E. (Princeton Junction, NJ); Forrest; Stephen R. (Princeton, NJ); Bulovic; Vladimir (Metuchen, NJ); Tian; Peifang (Princeton, NJ); Brown; Julie (Princeton, NJ), Assignee: Princeton University, US Patent 6403392
  58. US5811833: Electron transporting and light emitting layers based on organic free radicals. Thompson, Mark E. Issued: Sept. 22, 1998.
  59. US6242115: OLEDs containing thermally stable asymmetric charge carrier materials. Thompson, Mark E.; Koene, Bryan E.; Loy, Douglas E.; Issued June 12, 2001.
  60. US6,350,875: Synthesis of cyclooctatetraene derivatives and their use as electron transporters in organic light emitting diodes. Weber, William P.; Lu, Ping; Thompson, Mark E.; Hong, Haiping; Issued February 26, 2002.

61. K. Sayyah, "Method for transferring semiconductor device layers to different substrates", U.S Patent No. 6,287,891.
62. K. Sayyah, "Method for fabricating large area flexible electronics", U.S. Patent No. 6,291,266.

**APPENDIX B.**  
**LIST OF TECHNICAL JOURNAL PUBLICATIONS RESULTING FROM THIS**  
**DARPA-SPONSORED GRANT**

(cumulative, chronological, include papers in press or planned)

1. "Reliability and Degradation of Organic Light Emitting Devices", P. E. Burrows, V. Bulovic, S. R. Forrest, L. S. Sapochak, D. M. McCarty and M. E. Thompson, *Appl. Phys. Lett.*, **65**, 2922 (1994).
2. "Poly(P-Phenylene Vinylene)/Tris(8-hydroxy)Quinoline Aluminum Heterostructure Light Emitting Diode", C. C. Wu, J. K. M. Chun, P. E. Burrows, J. C. Sturm, M. E. Thompson, S. R. Forrest and R. A. Register, *Appl. Phys. Lett.*, **66**, 653 (1995).
3. "Organic Emitters Promise a New Generation of Displays", S. R. Forrest, P. E. Burrows and M. E. Thompson, *Laser Focus World*, 99 (Feb., 1995).
4. "Photoluminescence Efficiency and Absorption of Aluminum-Tris-Quinolate (Alq<sub>3</sub>) Thin Films", D. Z. Garbuzov, V. Bulovic, P. E. Burrows and S. R. Forrest, *Chem. Phys. Lett.*, **249**, 433 (1996).
5. "The Relationship Between Electroluminescence and Current Transport in Organic Heterojunction Light Emitting Devices", P. E. Burrows, Z. Shen, V. Bulovic, D. M. McCarty, S. R. Forrest, J. A. Cronin and M. E. Thompson, *J. Appl. Phys.*, **79**, 7991 (1996).
6. "Growth and Characterization of Electroluminescent Display Devices Using Vacuum-Deposited Organic Materials", S. R. Forrest, P. E. Burrows, and M. E. Thompson, chapter in Organic Electroluminescent Materials and Devices, S. Miyata and H. S. Nalwa, Eds., Gordon and Breach (1996).
7. "Transparent Organic Light Emitting Devices, ", G. Gu, V. Bulovic, P. E. Burrows S. R. Forrest and M. E. Thompson, *Appl. Phys. Lett.*, **68**, 2606 (1996).
8. "Temperature Dependence of Current Transport and Electroluminescence in Vacuum Deposited Organic Light Emitting Devices", Z. Shen, P. E. Burrows, V. Bulovic, D. M. McCarty, M. E. Thompson and S. R. Forrest, *Japan. J. Appl. Phys.-Lett*, **35**, L401 (1996).
9. "A Systematic Study of the Photoluminescent and Electroluminescent Properties of Petacoordinate Carboxylate and Chloro Bis-(8-Hydroxyquinaldine) Complexes of Gallium", L. S. Sapochak, P. E. Burrows, D. Garbuzov, D. M. Ho, S. R. Forrest and M. E. Thompson, *J. Phys. Chem.*, **100**, 17766 (1996).
10. "Vacuum-Deposited, Non-Polymeric Flexible Organic Light Emitting Devices", G. Gu, P. E. Burrows, S. Venkatesh, S. R. Forrest and M. E. Thompson, *Optics Lett.*, **22** 175 (1997).
11. "Color-Tunable Organic Light Emitting Devices", P. E. Burrows, S. R. Forrest, S. P. Sibley and M. E. Thompson, *Appl. Phys. Lett.*, **69**, 2959 (1996).
12. "High External Quantum Efficiency Organic Light Emitting Devices", G. Gu, D. Z. Garbuzov, P. E. Burrows, S. Venkatesh, S. R. Forrest and M. E. Thompson, *Optics Lett.*, **22**, 396 (1997).
13. "Achieving Full Color Organic Light Emitting Devices for Lightweight, Flat Panel Displays", P. E. Burrows, G. Gu, V. Bulovic, S. R. Forrest and M. E. Thompson, *IEEE Trans. Electron. Dev.*, invited, **44** 1188 (1997).

14. "Transparent Flexible Organic Light Emitting Devices", G. Gu, Z. Shen, P. E. Burrows and S. R. Forrest, *Adv. Mat.*, **9** 725 (1997).
15. "A Surface-Emitting Vacuum-Deposited Organic Light Emitting Device", V. Bulovic, P. Tian, P. E. Burrows, M. R. Gokhale, S. R. Forrest and M. E. Thompson, *Appl. Phys. Lett.*, **70** 2954 (1997).
16. "Three Color, Tunable Organic Light Emitting Device", Z. Shen, P. E. Burrows, V. Bulovic, S. R. Forrest, and M. E. Thompson, *Science*, **276**, 2009 (1997).
17. "Prospects and Applications for Organic Light Emitting Devices", P. E. Burrows, S. R. Forrest and M. E. Thompson, *Current Opinion in Solid State & Materials Science*, **2**, 236 (1997).
18. "The Stacked OLED (SOLED): A New Type of Organic Device for Achieving High Resolution Full Color Displays", S. R. Forrest, P. E. Burrows, Z. Shen, G. Gu, V. Bulovic and M. E. Thompson, *Synthetic Metals*, **91**, 9 (1997).
19. "Integration of Organic LEDs and Amorphous Si TFTs onto Flexible and Lightweight Metal Foil Substrates", C. C. Wu, S. D. Theiss, G. Gu, M. H. Lu, J. C. Sturm, S. Wagner and S. R. Forrest, *IEEE Electron Dev. Lett.*, **18**, 609 (1997).
20. "Low Pressure Organic Vapor Phase Deposition of Small Molecular Weight Organic Light Emitting Device Structures", M. A. Baldo, V. G. Kozlov, P. E. Burrows, S. R. Forrest, V. S. Ban, B. Koene and M. E. Thompson, *Appl. Phys. Lett.*, **71** 3033 (1997).
21. "Photolithographic Patterning of Vacuum-Deposited Organic Light Emitting Devices", P. F. Tian, P. E. Burrows and S. R. Forrest, *Appl. Phys. Lett.*, **71** 3197 (1997).
22. "Orange and Red Organic Light-Emitting Devices using Aluminum tris(5-hydroxyquinoxaline)", A. Shoustikov, Y. You, P. E. Burrows, M. E. Thompson, and S. R. Forrest, *Synthetic Metals*, **91**, 217 (1998).
23. "Thin Film Organic Light Emitting Devices and Lasers", S. R. Forrest, P. E. Burrows, V. Bulovic, V. Kozlov and M. E. Thompson, *Mat. Lett.*, invited, **34**, 103 (1998).
24. "See-through, multi-pixel organic emissive display," D. Yap, *Electronics Letters*, vol. 34, no. 9, 30 April 1998, pp. 915-916.
25. "Bright, Saturated Red-to-Yellow Organic Light Emitting Devices Based on Polarization Induced Spectral Shifts", V. Bulovic, A. Shoustikov, M. A. Baldo, E. Bose, V. G. Kozlov, M. E. Thompson and S. R. Forrest, *Chem. Phys. Lett.*, **287**, 455 (1998).
26. "A metal-free cathode for organic semiconductor devices", G. Parthasarathy, P. E. Burrows, V. Khalfin, V. G. Kozlov and S. R. Forrest, *Appl. Phys. Lett.*, **72** 2138 (1998).
27. "Light Emitting Devices Using Vacuum Deposited Organic Thin Films", P. E. Burrows, V. Bulovic, G. Gu, V. Kozlov, S. R. Forrest and M. E. Thompson, *Thin Solid Films*, **331**, 101 (1998).
28. "Control of Microcavity Effects in Full Color Stacked Organic Light Emitting Devices", P. E. Burrows, V. Khalfin, G. Gu and S. R. Forrest, *Appl. Phys. Lett.*, **73** 435 (1998).
29. "Hole Transporting Materials with High Glass Transition Temperatures for use in Organic Light Emitting Devices", D. F. O'Brien, P. E. Burrows, S. R. Forrest, B. E. Koene, D. E. Loy, and M. E. Thompson, *Adv. Mater.*, **10**, 1108 (1998).

30. "Weak Microcavity Effects in Organic Light Emitting Devices", V. Bulovic, V. B. Khalfin, G. Gu, P. E. Burrows, D. Z. Garbuzov and S. R. Forrest, *Phys. Rev. B*, **58** 3730 (1998).
31. "High Efficiency Phosphorescent Emission from Organic Electroluminescent Devices", M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, M. E. Thompson and S. R. Forrest, *Nature*, **395** 151 (1998).
32. "High-Efficiency, Low Drive-Voltage, Semitransparent Stacked Organic Light Emitting Device", G. Gu, V. Khalfin and S. R. Forrest, *Appl. Phys. Lett.*, **73**, 2399 (1998).
33. "New Approaches to Organic Light Emission", S. R. Forrest, M. A. Baldo, V. Bulovic, P. E. Burrows, D. O'Brien, G. Parthasarathy, S. Sibley, A. Shoustikov, M. E. Thompson and Y. You, *Polymer Preprints*, **39**, 992 (1998).
34. "Making Light of It", S. R. Forrest, P. E. Burrows, M. E. Thompson, *Chem. & Ind.*, invited, 1022 (Dec. 21, 1998).
35. "A Metal-Free, Full-Color Stacked Organic Light Emitting Device", G. Gu, G. Parthasarathy and S. R. Forrest, *Appl. Phys. Lett.*, **74**, 305 (1999).
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**APPENDIX C.**  
**LIST OF PROFESSIONAL PERSONNEL ASSOCIATED WITH THIS EFFORT**

Persons who contributed to technical work on this effort are listed by institution below.

**Hughes Research Laboratories (HRL Labs):**

Keyvan Sayyah

**Princeton University:**

Stephen Forrest, Chihaya Adachi, Marc Baldo, Vladimir Bulovic, Paul Burrows,  
Vladimir Kozlov, Sven Möller, Diarmuid O'Brien, Martin Pfeiffer, Zilan Shen,  
Shashank Agashe, Gong Gu, Changsoon Kim, Daijue Tang, Jiangeng Xue

**Universal Display Corporation**

Steve Abramson, Julie Brown, Vladimir Bulovic, Mike Hack, Janice Mahon, Sokhanno Mao,  
Lech Michalski, Kamala Rajan, Franky So, Ken Urbanik, Teddy Zhou

**University of Southern California**

Mark Thompson, Feras Abdel-Razzaq, Vadim Adamovich, Jason Brooks, Steven Cordero,  
Jon Cronin, Peter Djurovich, Haiping Hong, Raymond Kwong, Shannon Koene, Bryan Koene,  
Dmitry Kolosov, Sergey Lamansky, Douglas Loy, Drew Murphy, Scott Sibley,  
Andrei Shousitkov, Jing Tian, Yujian You

**APPENDIX D.**  
**LIST OF ADVANCED DEGREES AWARDED**  
**FOR RESEARCH ACCOMPLISHED UNDER THIS GRANT**

Advanced degrees awarded in association with research sponsored under this grant are listed below by institution in the following format: (date, recipient, type of degree, thesis title).

**Princeton University:**

1998, Zilan Shen, Ph.D., "Organic Light Emitting Devices and the Theory of Excited States in Organic Nanostructures"

1999, Gong Gu, Ph.D., "Multicolor Organic LEDs"

1999, Vladimir Bulovic, Ph.D., "Organic Light Emitters

2001, Marc Baldo, Ph.D., "Optical and Electronic Properties of Amorphous Organic Semiconductors"

**University of Southern California:**

1999, Shannon Koene, Ph.D, "Hole Transporting Dendrimers and Their Use in Organic Light Emitting Diodes"

2000, Raymond Kwong, Ph.D., "Electrophosphorescence in Organic Light Emitting Diodes"

2000, Douglas E. Loy, Ph.D., "Molecular hole transporting materials for organic light emitting diodes"

2001, Dmitry Kolosov, Ph.D., "1,8-Naphthalimides as Novel Materials for Phosphorescent Organic Light Emitting devices and Degradation Studies of Transparent Light Emitting Devices"

2001, Sergey A. Lamansky, Ph.D., "Chemistry of novel iridium and platinum ortho-metalated complexes and decaarylplumbocenes for organic light emitting diodes"

2001, Adrei Shoustikov, Ph.D., "Fluorescent and Phosphorescent Dyes in Organic Light-Emitting Diodes"

2002, Feras Abdel Razzaq, Ph.D., "Phosphorescence in Organic Light Emitting Diodes"

**APPENDIX E.**  
**MAY 3, 2002 FINAL REVIEW MATERIALS**

# Vacuum Deposited Organic Light Emitting Devices on Flexible Substrates

*"what a long, strange trip it's been"*

Final Program Review  
Princeton University

May 3, 2002

## Program Objective

Demo PM & AM flexible displays by pushing the state of the art in OLED technology using SOLEDs, FOLEDs, OVPD, lasers and organic transistors.

# Vacuum Deposited Organic Light Emitting Devices on Flexible Substrates

**Support:** DARPA (F33615-94-1-1414)

**Program Managers:** Gurdial Saini & Darrel Hopper

**Agent:** Wright Patterson AFB

**Dates:** 6/13/94 - 4/30/02

### Team:

Princeton University (S. Forrest)

HRL (K. Sayyah) - End Dec. 31, 00

Universal Display Corporation (J. J. Brown) - End Dec. 31, 00

University of Southern California (M. E. Thompson)

## Team Responsibilities

- **Princeton:** Develop flexible, transparent, stacked and ultrahigh efficiency OLEDs and packaged display pixel arrays. Initial reliability testing. Organic transistors and roll-to-roll processing demonstrations.
- **USC:** Organic materials development for high reliability, efficient, saturated color.
- **HRL:** Si TFT AM development on glass and flexible substrates using lift-off. Qualification for DoD and civilian applications.
- **UDC:** Reliability studies of AM & PM flexible displays. Display manufacturing development and scale-up. Formation of strategic alliances.

## Specific Objectives

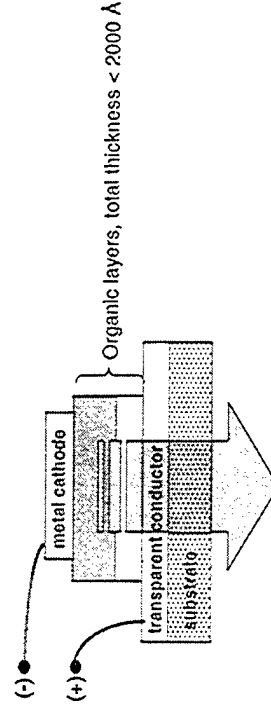
- Demo. flexible, ultralight weight, AM displays. (x)
- Demo. RGB SOLED pixel with true color (✓)
- Demo. high efficiency OLEDs with luminescence in the R, G & B using vacuum-deposited organics (✓)
- Demo. scalability to large substrates (✓)
- Demo. photolith patterning of high resolution pixels (✓)
- Demo. OLED reliability (✓)
- Demo. organic-TFTs for displays
- Develop methods to select optimal materials for high efficiency displays (✓)
- Refine processes for prototype and manufacture (✓)

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## Accomplishments

- Demo'd transparent, true color patterned SOLEDs
  - ✓ Developed full, *quantitative* understanding of microcavity effects
- Demo'd efficient R, G, B color emission
  - ✓ Demo'd electrophosphorescent efficiencies in red and green (19%, int. eff. ~87%)
  - ✓ Demo'd phosphor-sensitized fluorescence with efficiencies of 8%.
  - ✓ Extremely long operational lifetimes found for some phosphors
- Demo'd efficient TOLEDs for head-up, integrated apps.
- Tech. transfer to UDC (facility on line) & HRL
- Demonstrated method for micropatterning of displays: cold-welding followed by lift-off
- Demonstrated growth of OLEDs via OVPD
  - ✓ Equipment manufacturer building large scale production tools

## Benefits of OLEDs

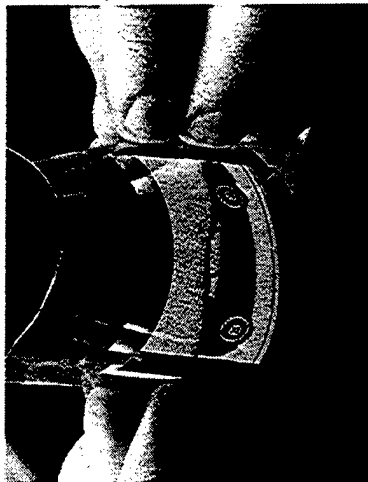


- can be prepared on any substrate - active materials are amorphous

## Technology Transfer

- ~40 Patents pending
  - ✓ Architectures, materials, packages, phosphorescence, transistors, patterning
  - ✓ ~50 issued: FOLED, TOLED and SOLED parent case, phosphorescence, patterning, laser, vacuum and OVPD deposition basic patents.
  - ✓ All patents filed globally, with exclusive rights to UDC.
- Established strong ties with potential manufacturers of equipment and panels
- Prototyping and Tech. Transfer facility opened by Universal Display- Significant resource leveraging and customer interest

## Flexible, Passive Matrix OLED Display



Courtesy: Universal Display Corp.

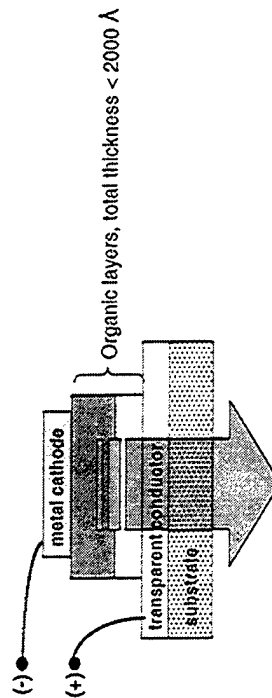
Flexibility is a transformational advantage of OLEDs.

But significant challenges remain:

- Lifetime must improve
- Conformal vs flexible
- Mechanical ruggedness

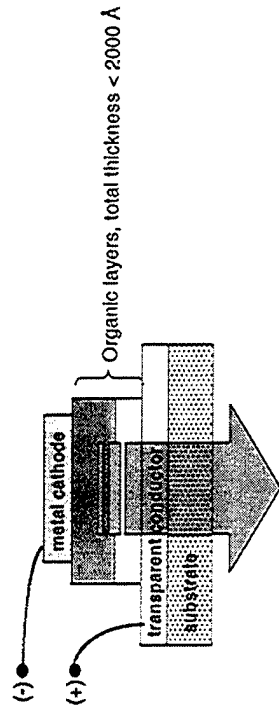
128x64 pixels, 400x500 $\mu$ m each  
Display dimension: 2"x3"  
Full motion video

## Benefits of OLEDs



- readily tuned color and electronic properties via Chemistry
- can be transparent when off

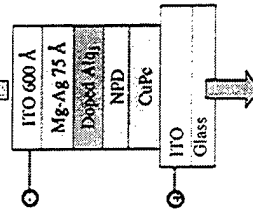
## Benefits of OLEDs



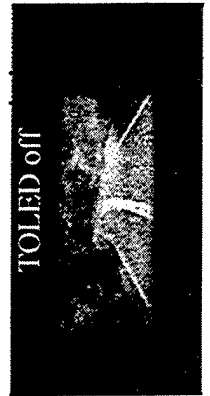
- low cost materials and fabrication methods, scalable to large area

## Transparent OLEDs (TOLEDs)

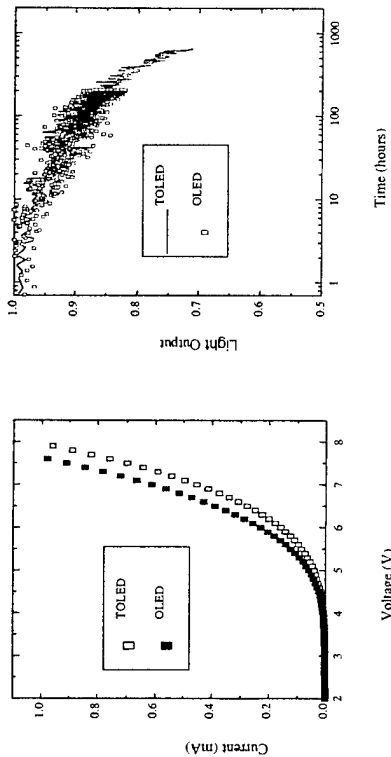
- Devices can be > 90% transparent
- Thin metal or electron injection layer is capped with ITO
- Transparent cathode can also be used



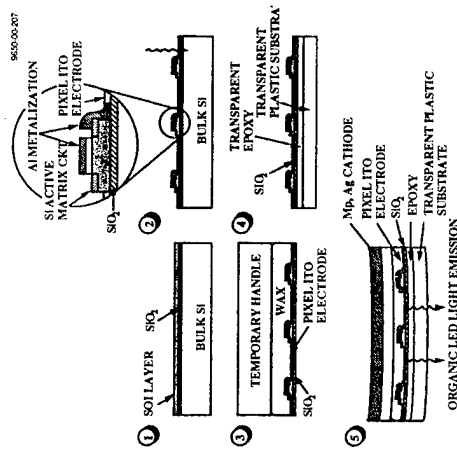
Bulovic et al., Nature 1996



## TOLED Current-Voltage and Lifetime Characteristics



## Schematic of Flexible AM-OLED Fabrication Process



## Sony 13 inch AMOLED-TFT Display

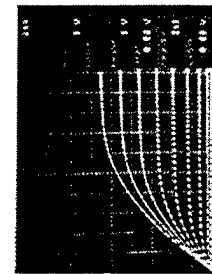
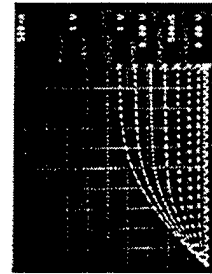
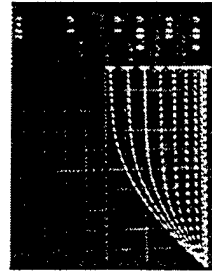


800x600 pixels  
Full Color  
Top emission

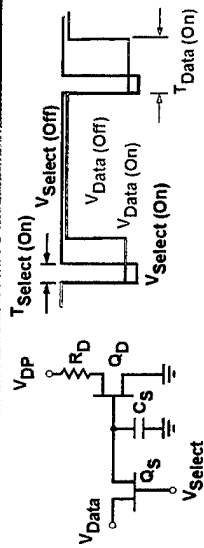


## Characterization of Bonded-SOI PMOS Transistors (2)

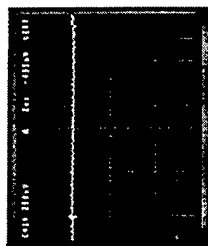
### PMOS Bonded-SOI I-V Characteristics



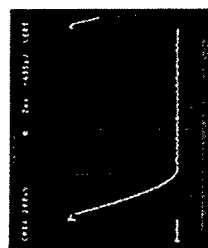
# Characterization of Bonded-SOI Two Transistor Active Matrix Circuit (Resistor Load)



$V_{\text{Select (On)}} = -12 \text{ V}$   $C_S = 0.5 \text{ pF}$   $V_{\text{Data (On)}} = -10 \text{ V}$   
 $T_{\text{Select (On)}} = 100 \text{ } \mu\text{s}$   $T_{\text{Frame}} = 16 \text{ ms}$   $T_{\text{Data (On)}} = 500 \text{ } \mu\text{s}$

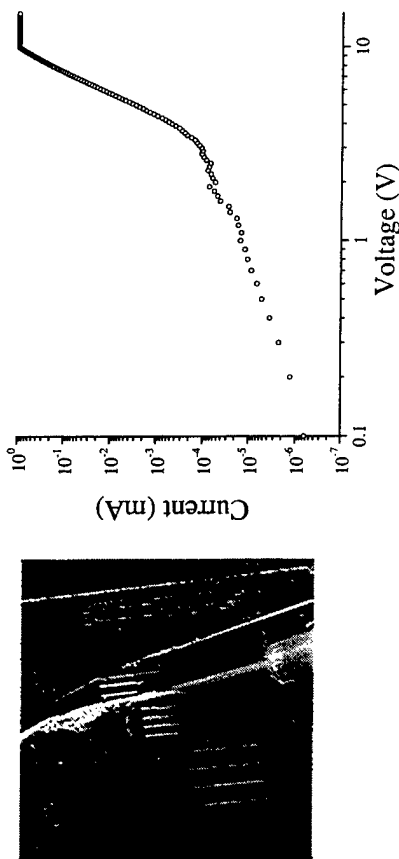


$V_{\text{Select (Off)}} = 0 \text{ V}$



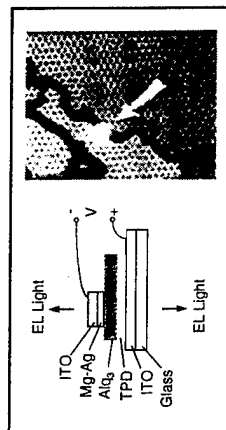
$V_{\text{Select (Off)}} = -1.6 \text{ V}$

Wafer	$C_S$ [pF]	$\Delta I_L / I_L (\%)$
A-1	0.5	2%
A-1	1.1	<1%
A-1	11.0	<0.5%
A-2	0.5	<1%
A-2	1.1	<1%
A-2	11.0	<0.5%
A-3	0.5	2%
A-3	1.0	<0.5%
A-3	11.0	<0.5%
A-4	0.5	3%
A-4	1.1	2%
A-4	11.0	<0.5%
A-5	0.5	<0.5%
A-5	1.1	<0.5%

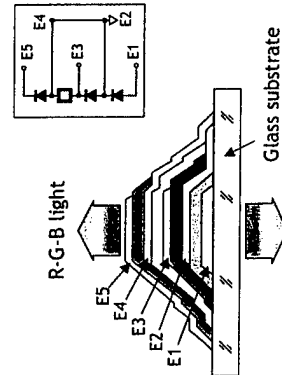


Data Summary for TOLEDs on Hughes Si

## Transparent & Stacked Organic Light Emitting Devices for Full Color Generation

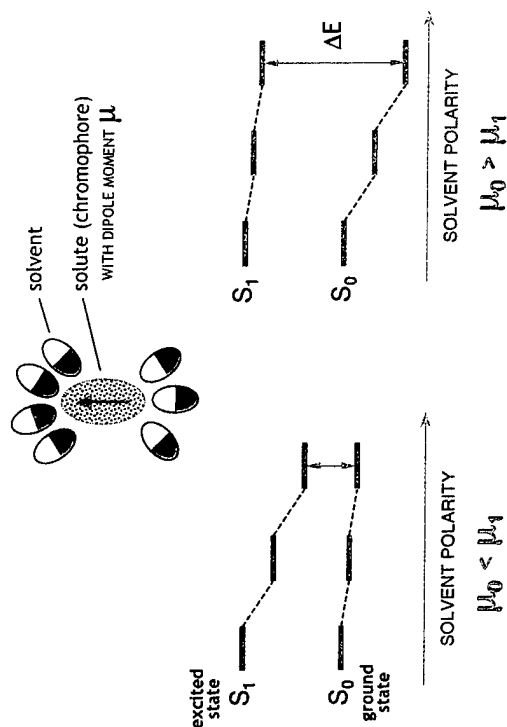


V. Bulovic, et al., *Nature*, 380 29 (1996)



G. Parthasarathy, et al., *Adv. Mater.*, 11, 907 (1999).

## Influence of $\mu_0$ and $\mu_1$ on Chromatic Shift Direction





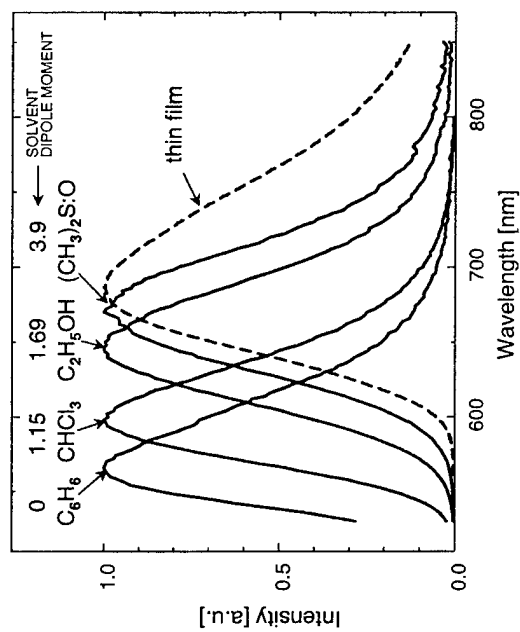


Figure 3. Bulović et al.

### Peak EL of DCM2 in Different Hosts

Bulović et al., Chem. Phys. Lett. submitted (1999).

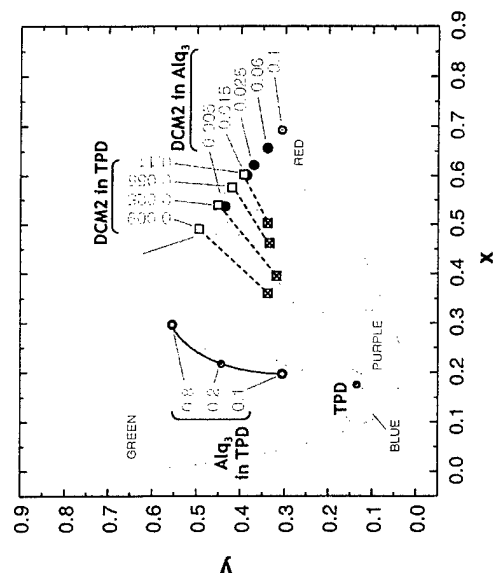
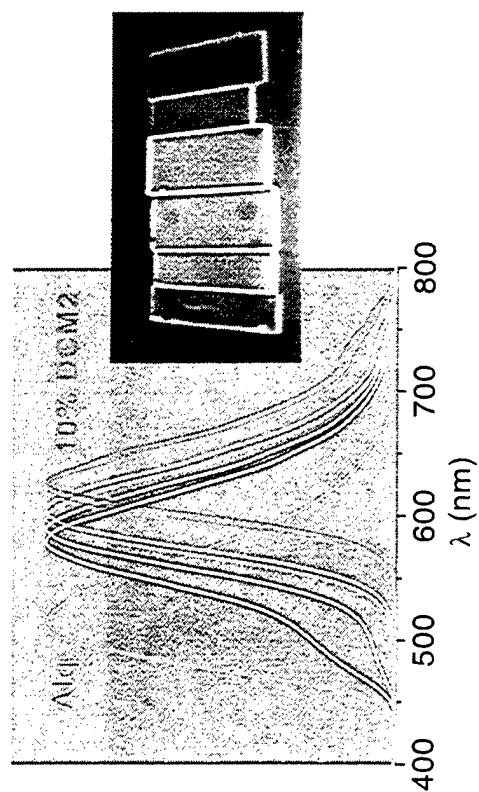
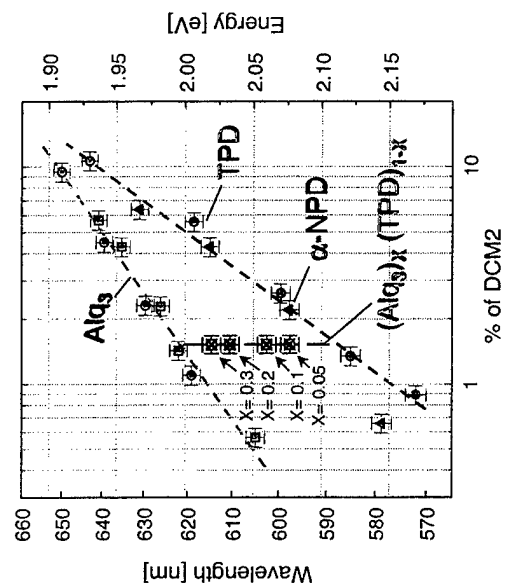
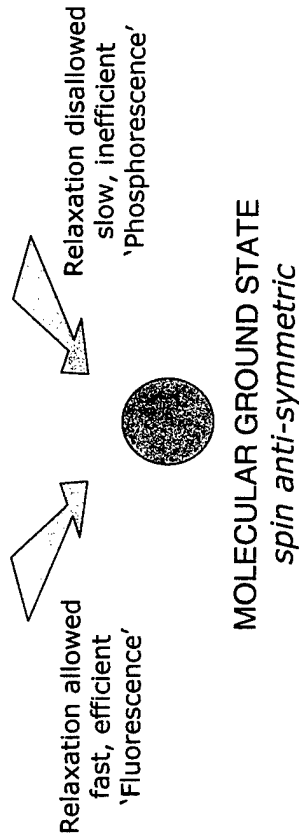
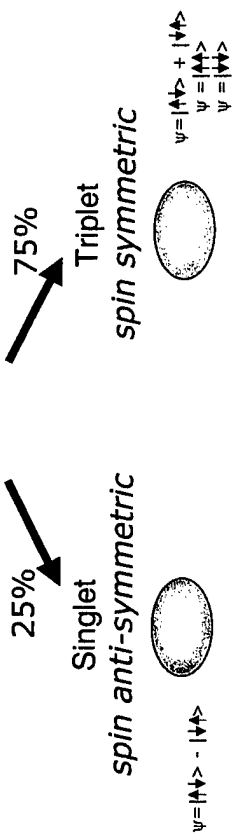
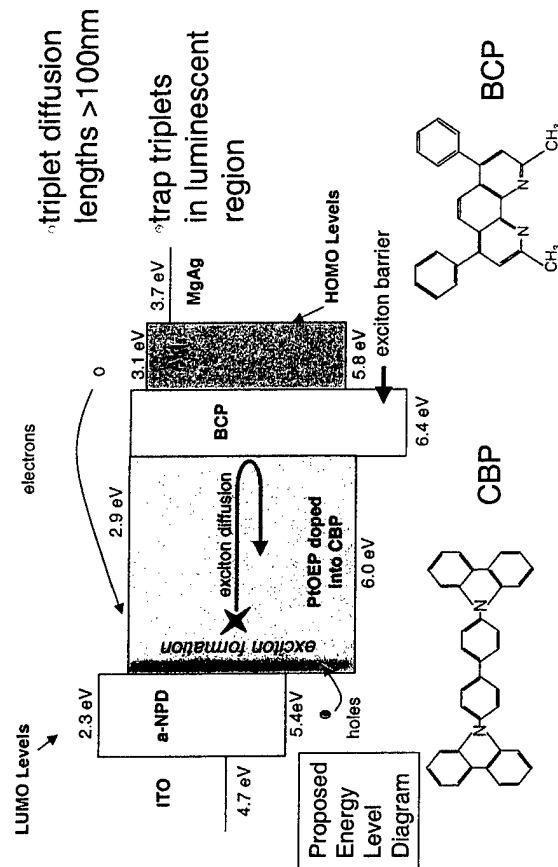


Figure 9. Bulović et al.

## MOLECULAR EXCITED STATES AFTER ELECTRICAL EXCITATION

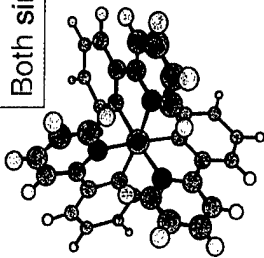


## Electrophosphorescent device structure



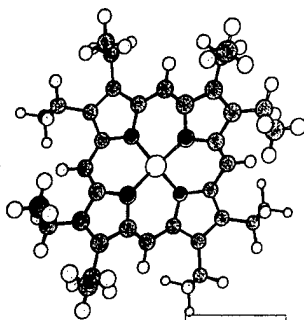
Phosphorescence enhanced by mixing the singlet and triplet excited states  
eg: spin orbit coupling via heavy metal atom (Pt or Ir)

Both singlets and triplets are harvested!



*fac tris(2-phenylpyridine) iridium*  
**Ir(ppy)<sub>3</sub>**

green emission  
external quantum efficiency ~19%  
phosphorescent lifetime ~0.5μs

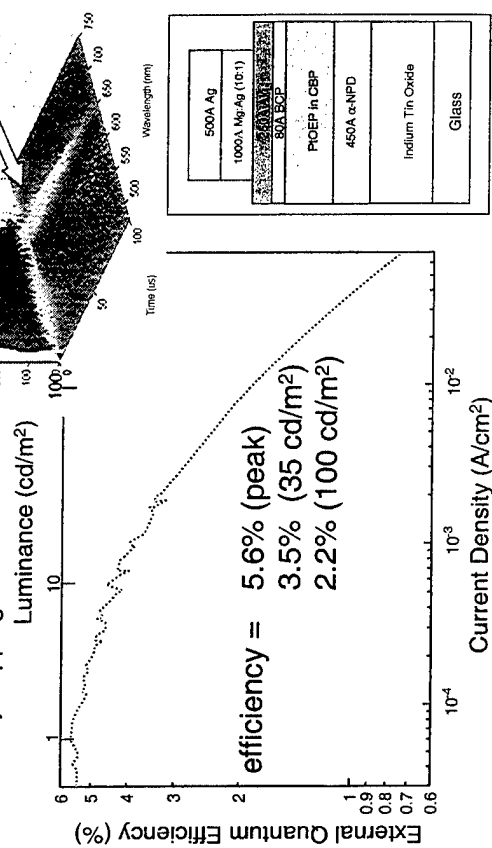


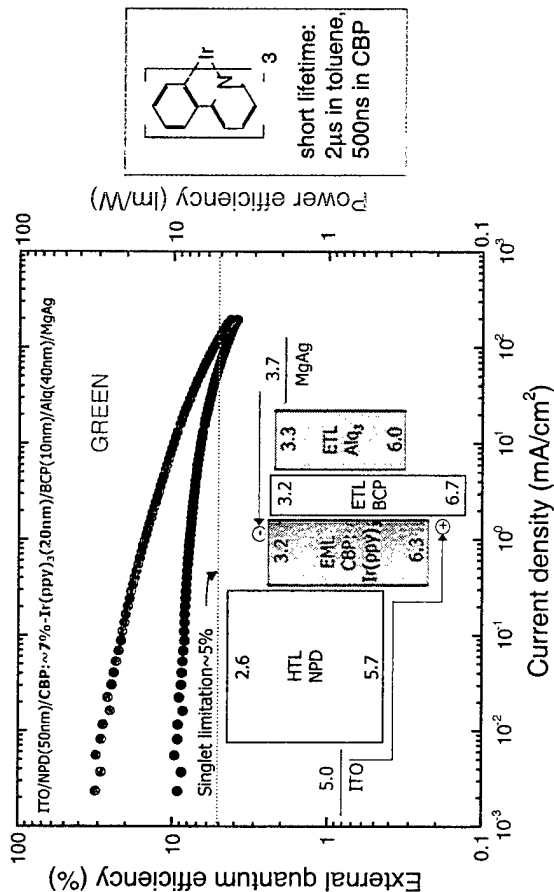
*platinum octaethylporphyrin*  
**PtOEP**

red emission  
external quantum efficiency ~6%  
phosphorescent lifetime ~70μs

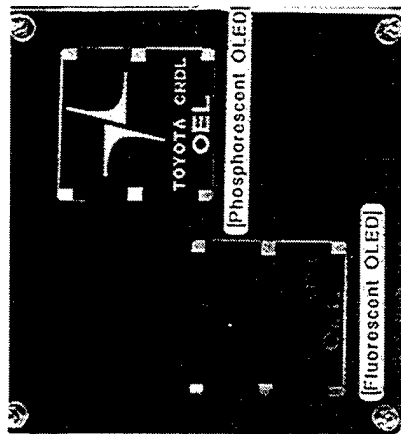
## 6% PtOEP in CBP

- Exciton blocker increases eff. by 50%
- Roll off at modest luminance levels
- Transfer by trapping





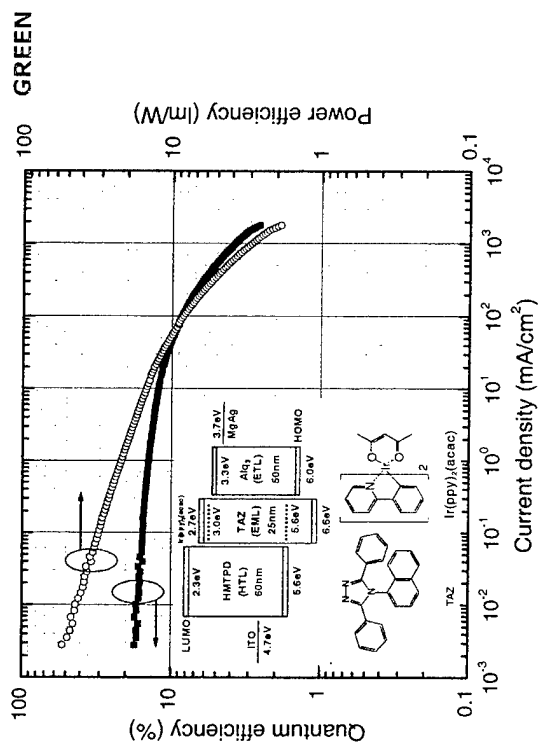
OLED panels of fluorescence and phosphorescence



Conventional OLED Phosphorescent OLED

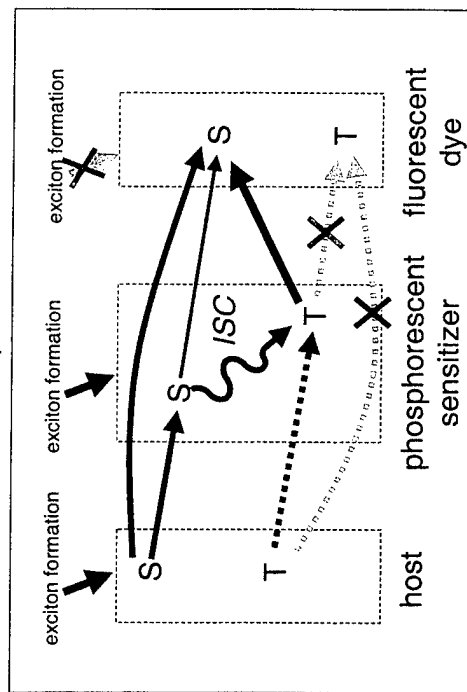
2001 MRS spring meeting, San Francisco, Paper C4.3

TOYOTA CENTRAL R&D LABS., INC.

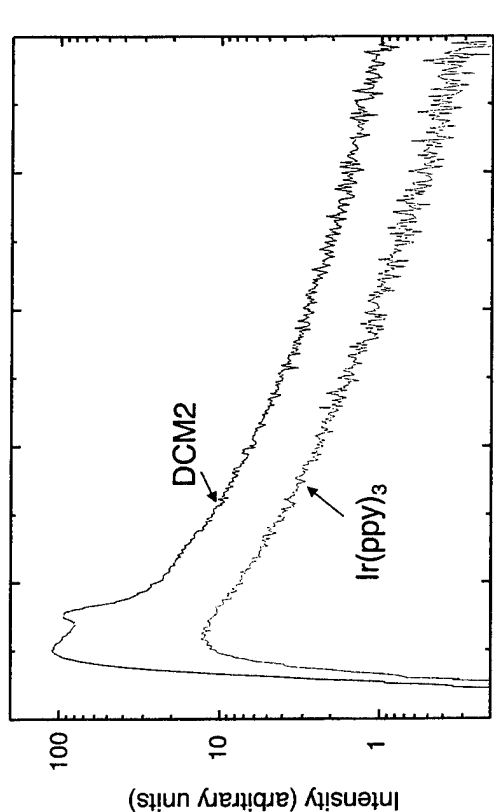


TRIPLET - SINGLET TRANSFER

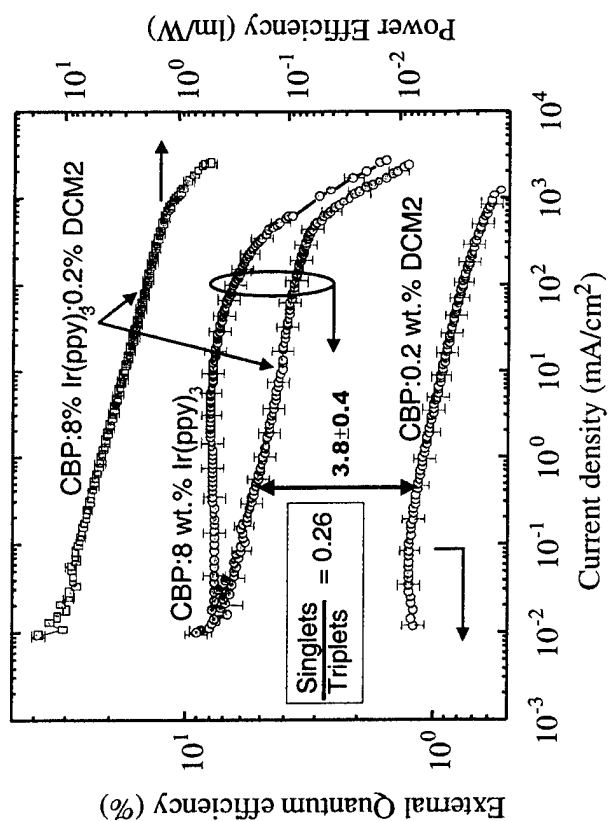
- Need separation between phosphorescent donor and fluorescent acceptor to prevent direct Dexter transfer to fluorescent triplet state
- Transfer possible for radiative triplet states



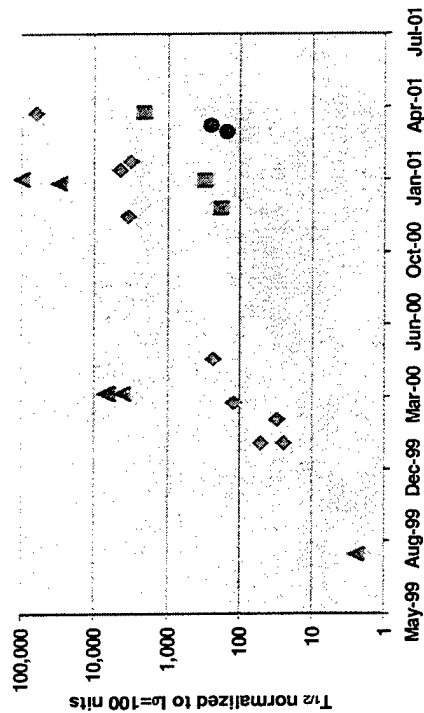
## OLED Transient Response



◇ Delayed DCM2 fluorescence confirms sensitizing action of Ir(ppy)<sub>3</sub>



## Phosphorescent OLED Lifetime



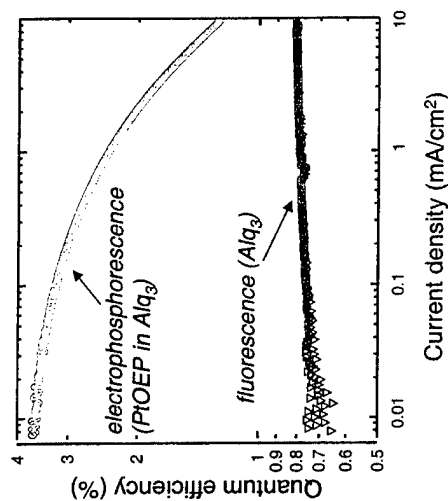
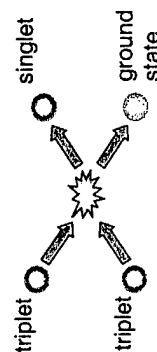
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## PHOSPHORESCENT EFFICIENCY DEGRADES WITH CURRENT DENSITY

*Is it saturation of phosphorescent sites?*

Current densities too low.  
Should be proportional to  $1/J$  but actually closer to  $1/\sqrt{J}$ .

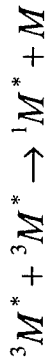
*Or T-T annihilation?*



*Can the degradation be minimized?*

## THEORY

T-T annihilation destroys two triplets and creates a singlet



Transient model: 
$$\frac{d[^3M^*]}{dt} = -\frac{[^3M^*]}{\tau} - k_q[^3M^*]^2 + \frac{J}{qd}$$

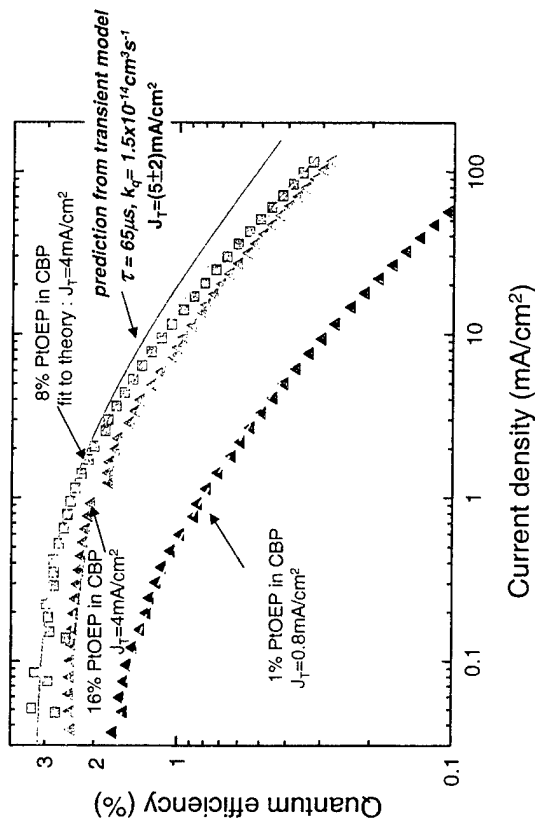
$\tau$ : triplet lifetime  
 $k_q$ : T-T annihilation rate  
 $J$ : current density  
 $d$ : thickness of active layer

Transient solution: 
$$[^3M^*(t)] = \frac{[^3M^*(0)]}{(1 + [^3M^*(0)]\tau k_q)e^{t/\tau} - [^3M^*(0)]\tau k_q}$$

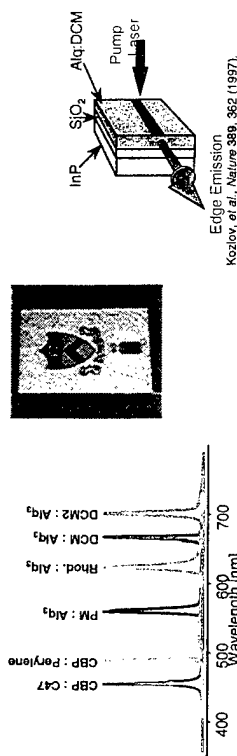
Steady state solution: 
$$\frac{\eta}{\eta_0} = \frac{J_T}{4J} \left( \sqrt{1 + 8 \frac{J}{J_T}} - 1 \right)$$
  
 $\eta$ : quantum efficiency  
 $\eta_0$ : max efficiency

Threshold current density: 
$$J_T = \frac{2qd}{k_q \tau^2}$$
  
(for  $\eta = \eta_0/2$ )

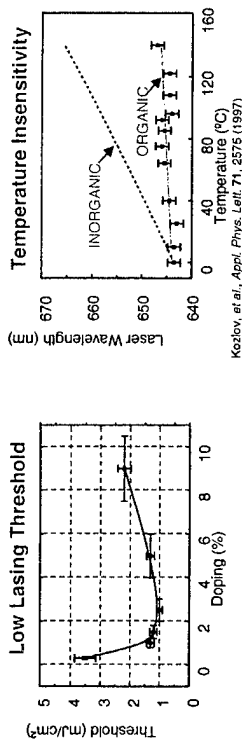
## PREDICTION FROM TRANSIENT MODEL MATCHES MEASUREMENT



## Organic Lasers

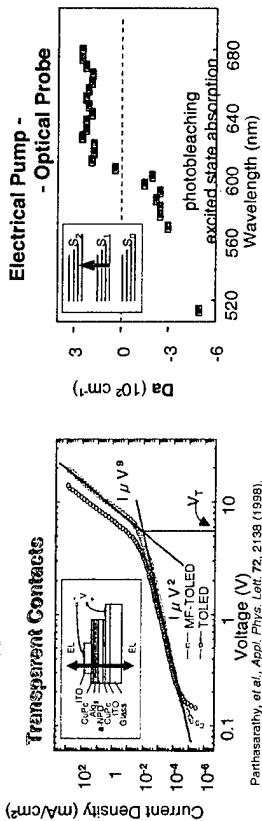
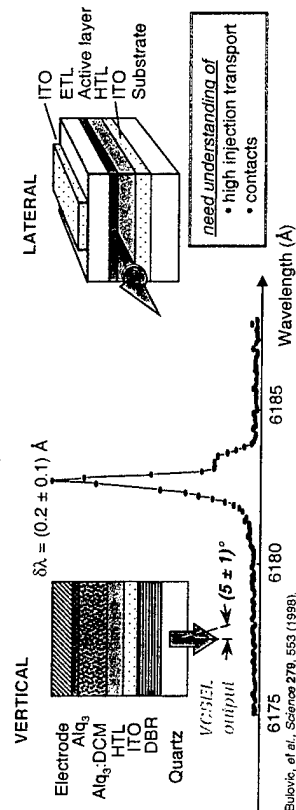


- Motivation**
- Material Tunability
  - Freedom from Epitaxial Limitations
  - Natural Quantum Dots



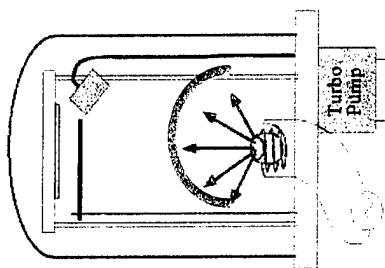
## Organic Lasers

### Electrically Pumped Structures



## Vacuum Deposition

$10^{-6}$  -  $10^{-11}$  Torr



### Advantages

- Simple
- Precise (monolayer) thickness control

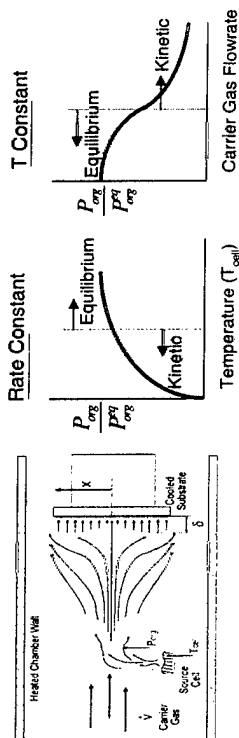
### Disadvantages

- Inefficient use of material
- Difficult to control dopant concentration
- Uneven deposition rate
- Chamber contamination and dust

→ Difficult to scale-up throughput

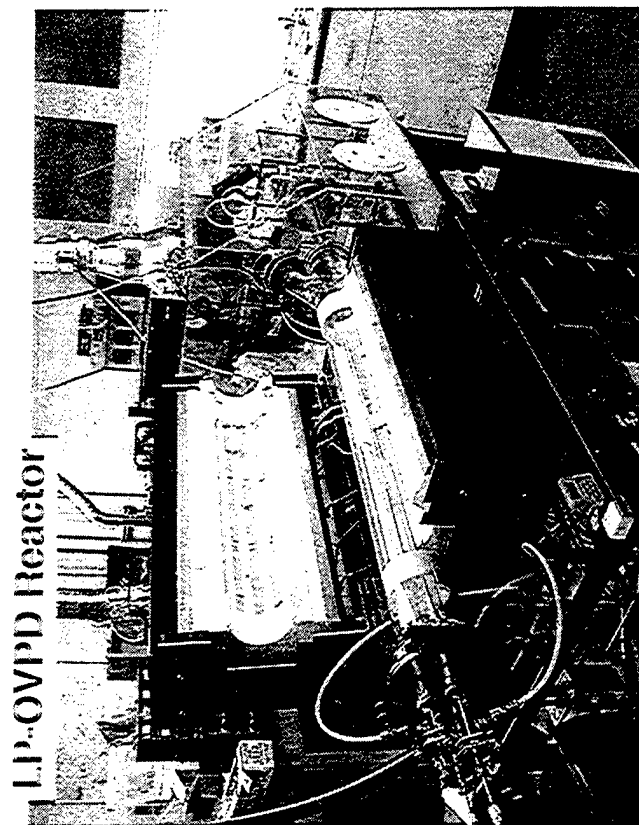
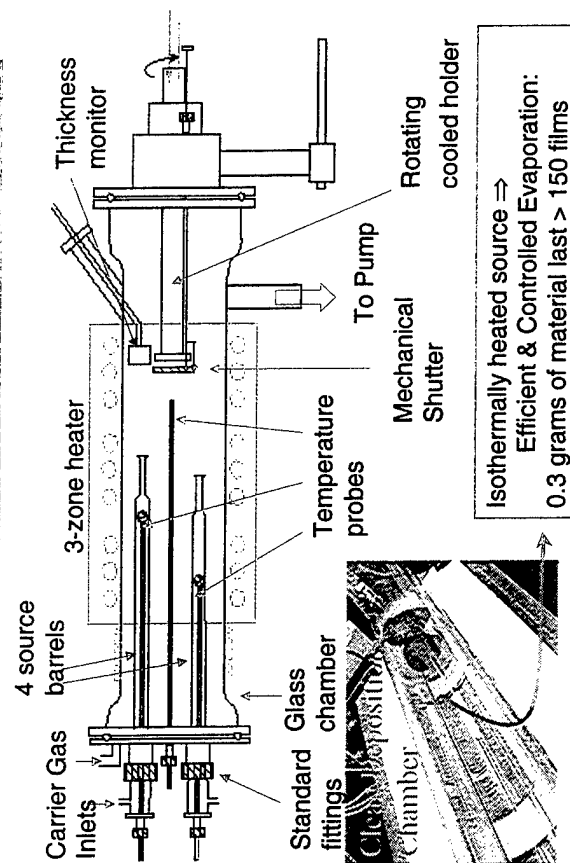
## Organic Vapor Phase Deposition

Chamber pressure: 0.1-10 Torr



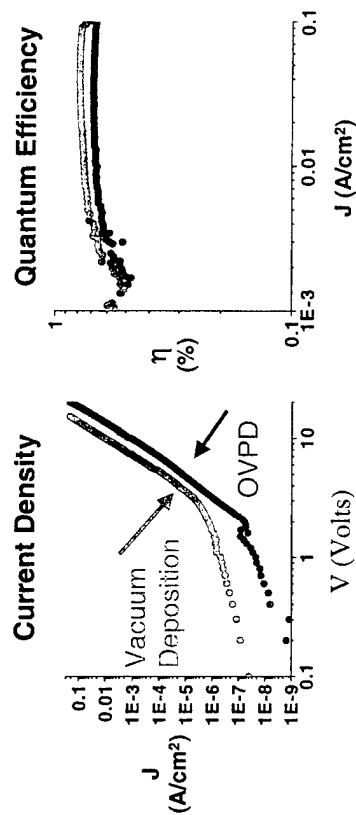
- Controlled and accurate doping
- Dust free chamber
- Efficient materials use
- Control of film crystal structure

## OVPD: Deposition System Design

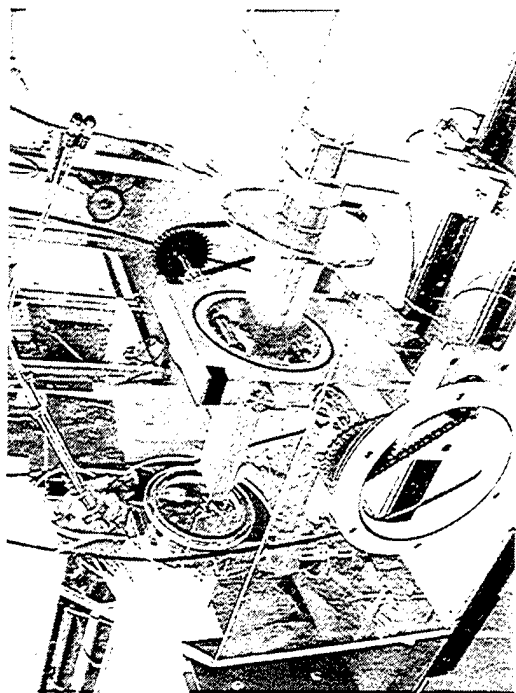


## OVPD vs. Vacuum Deposition: OLEDs

MgAg	1000 Å
Alq <sub>3</sub>	500 Å
α-NPD	500 Å
ITO	1000 Å
Glass/Plastic	1 mm

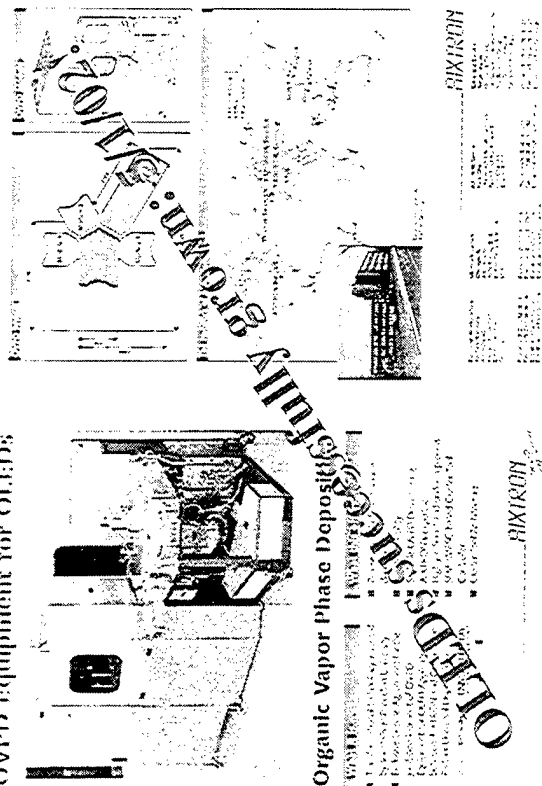
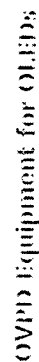
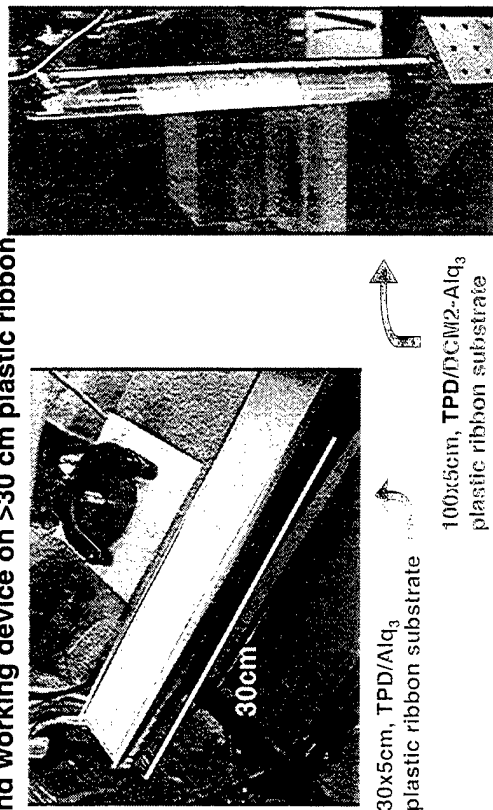


### OVPD for Roll-to-Roll Deposition:

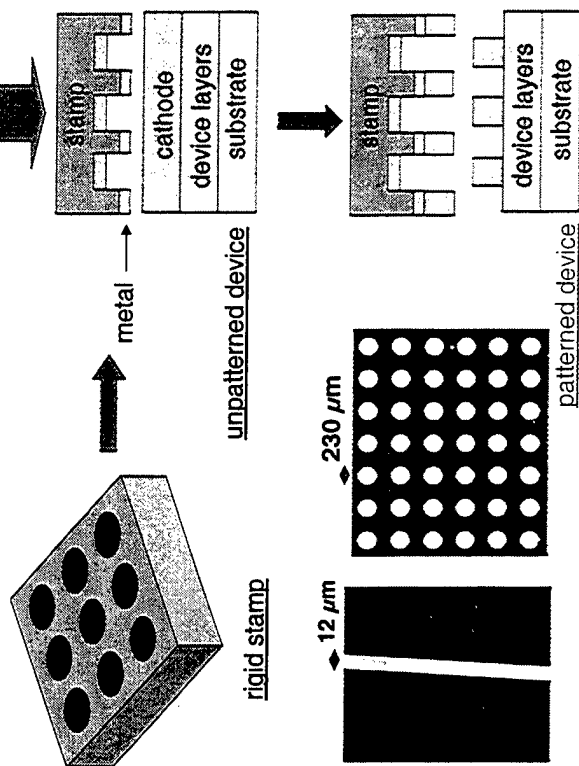


## OVPD for Roll-to-Roll Deposition of OLEDs:

## 1st demonstrated OLED heterostructure and working device on >30 cm plastic ribbon

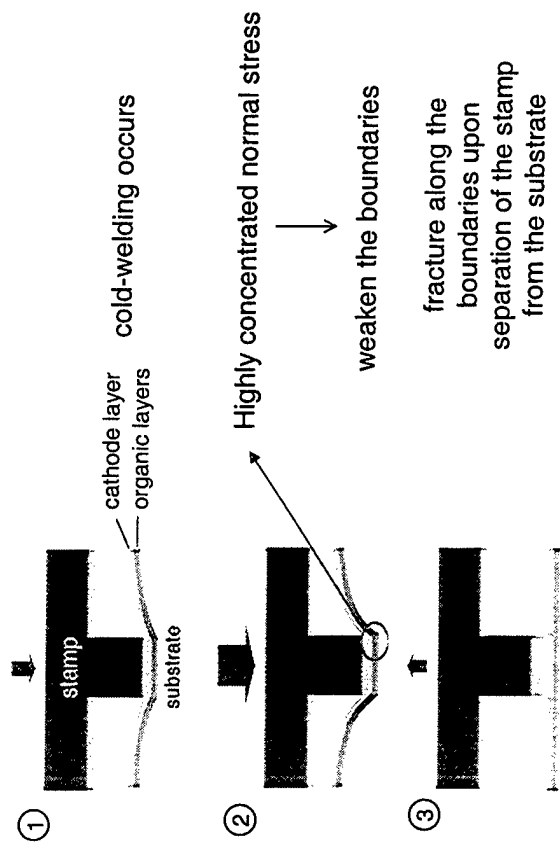


# Direct nanopatterning by cold-welding followed by lift-off

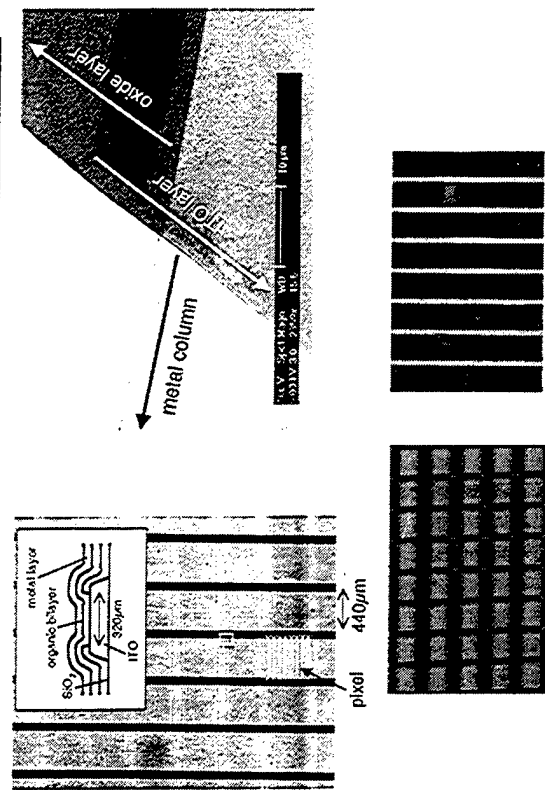


62

## mechanism

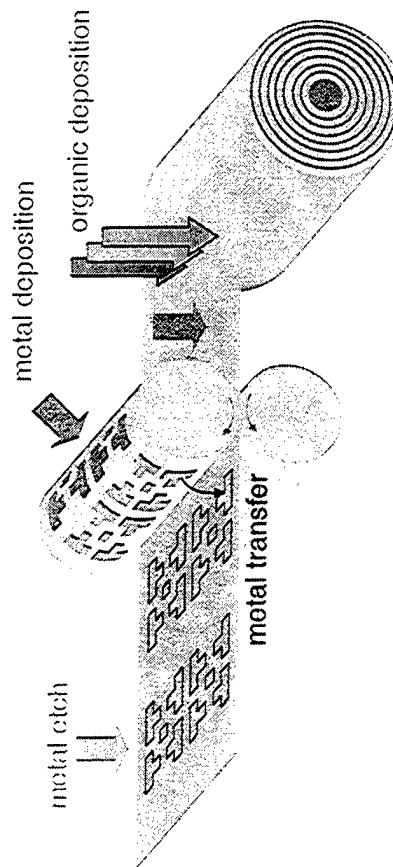


# Display Fabrication Using Cold-Welding Followed by Lift-Off



Passive-Matrix OLED Display in Operation

## OVPD & Cold-Welding: web-processing of organic devices



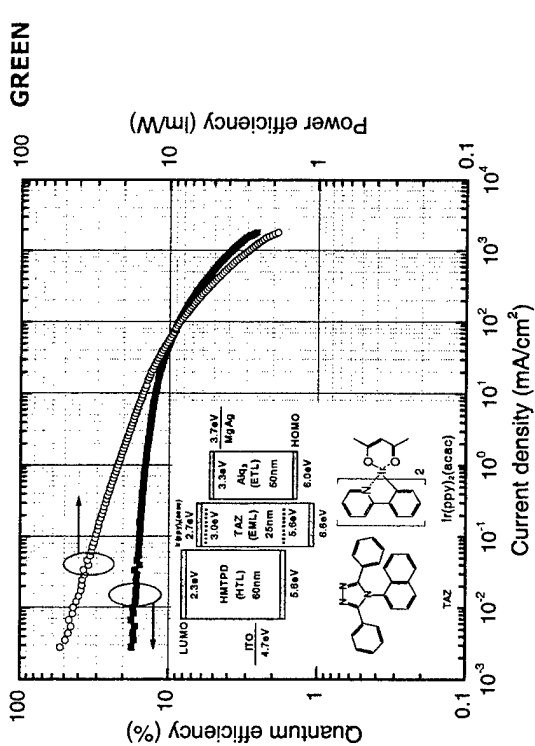


# Recent advances in small molecular weight displays

Stephen Forrest  
Department of Electrical Engineering  
Princeton University

Princeton University

***Ir(ppy)<sub>2</sub>(acac) doped ETL (Triazole) ( $\eta_{ext}=19\%$ ,  $\eta_{int}=87\%$ )***



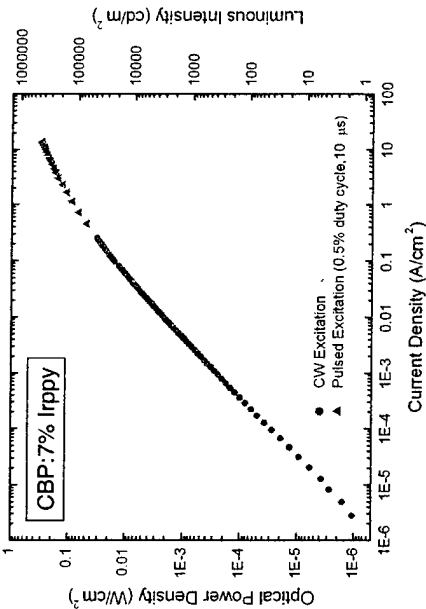
Princeton University

# Accomplishments

- Achieved high brightness greens and deep blues
- Demonstrated efficient phosphor polymer devices
- Demonstrated efficient, simplified white OLEDs
- Modeled and demonstrated high resolution patterning by OVPD
- Developed “unified model” of current-voltage characteristics of OLEDs
- Demonstrated cold-welding by metal addition

Princeton University

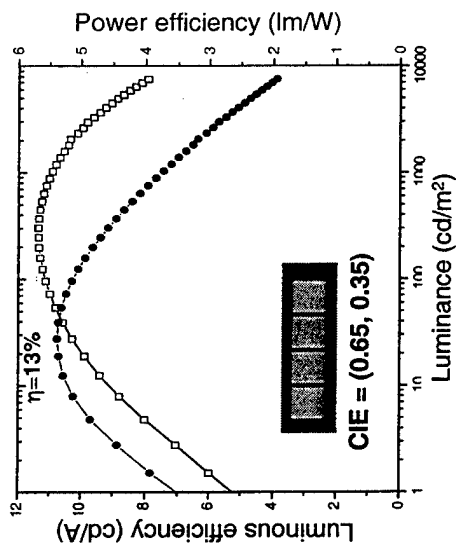
High Brightness Phosphorescent Devices



Peak brightness of a 13% efficient CBP:7% Irppy device approaches  
5 x 10<sup>5</sup> cd/m² and 0.3 W/cm²  
Compare to a 1.7% efficient CBP device with 6 x 10<sup>4</sup> cd/m² and an optical  
power density of 0.2 W/cm² under the same excitation

Princeton University

## Red PHOLED Performance

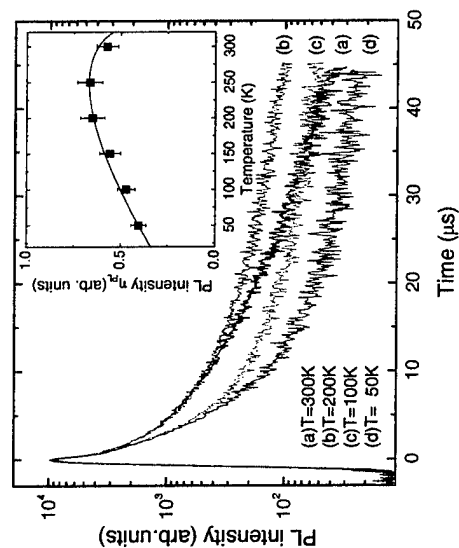


cd/m <sup>2</sup>	cd/A	V
100	11.2	6.8
300	11.4	7.8
500	11.3	8.3

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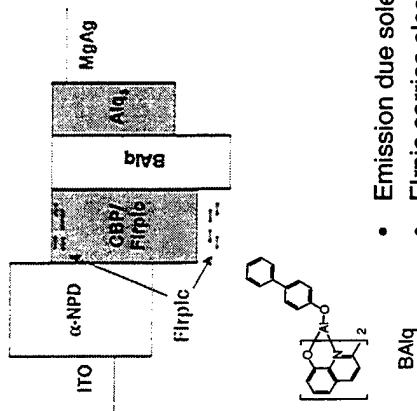
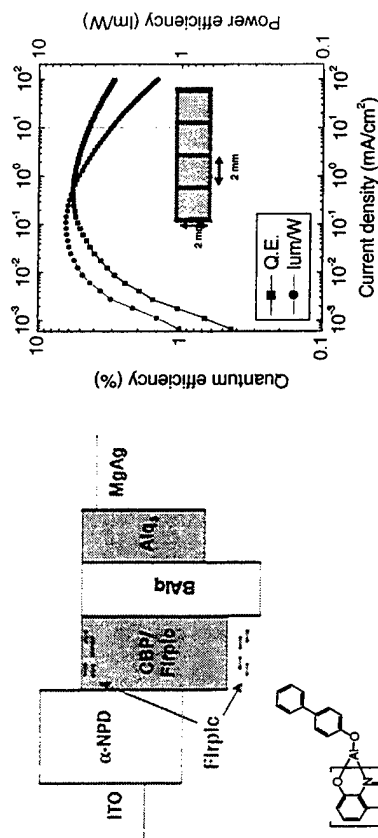


## Temperature Dependent PL of Flr(pic)



Princeton University

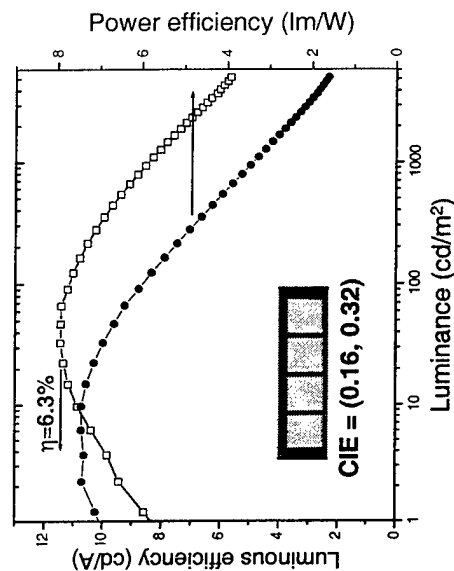
## Blue Electrophosphorescence from Flrpic/CBP



- Emission due solely to phosphorescent dopant
- Flrpic carries electrons in CBP
- Efficiency = 5.5%, > 5 lum/W, 12 cd/A at 100 cd/m<sup>2</sup>

Princeton University

## Blue PHOLED Performance

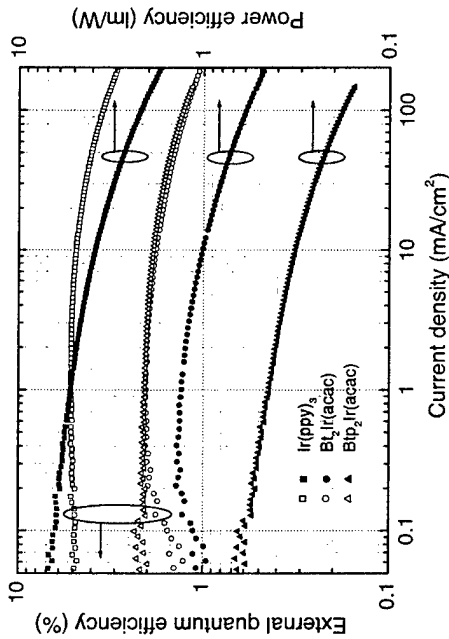


cd/m <sup>2</sup>	cd/A	V
100	11.1	5.8
500	9.6	7.2
1000	8.5	8.3

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## Polymer based Electrophosphorescence



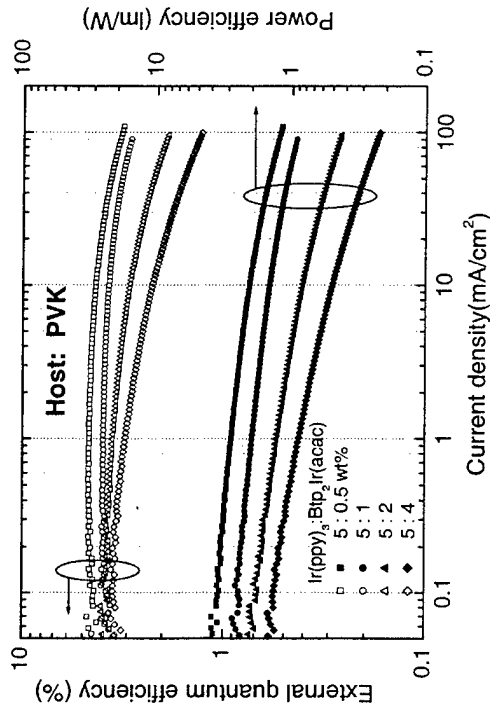
Efficiencies considerably less than small molecules:  
 Due to low lying triplet and defect states in PVK host defeating energy transfer

## Summary of Efficiencies in EP-OLEDs

phosphor	host	$\Phi$	$J = 1 \mu\text{A}/\text{cm}^2$						$J = 1 \text{ mA}/\text{cm}^2$			
			$\eta_P$ (lm/W)	$\eta_P$ (lm/W)	$\eta_{\text{Oext}}$	$\eta_{\text{Oint}}$	$V_{\chi}/V$	$\eta_P$ (lm/W)	$\eta_{\text{Oext}}$	$\eta_{\text{Oint}}$	$V_{\chi}/V$	
ppv <sub>2</sub> Ir(acac)	TAZ	530	60	60	0.19	0.87	0.60	20	0.15	0.68	0.25	
	CBP	170	4	4	0.07	0.32	0.34	2.2	0.06	0.27	0.22	
Flrpic	CBP	260	1.3	1.3	0.006	0.027	0.83	5.0	0.057	0.23	0.34	
PtOEP	CBP	60	0.3	0.3	0.056	0.23	0.09	0.2	0.042	0.19	0.08	

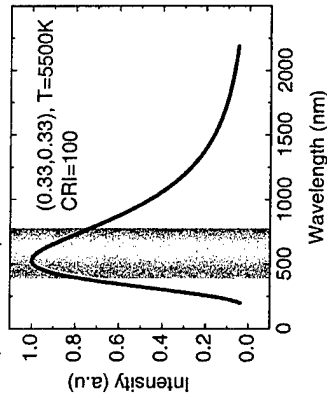


## 2.5 times enhancement of red efficiency by phosphor sensitization

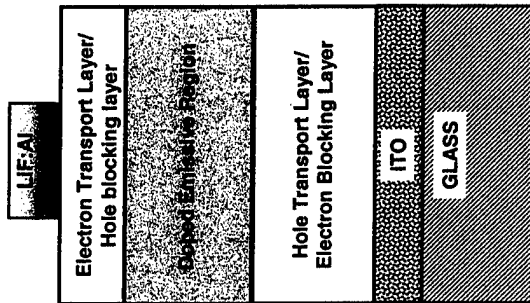


## Organic White Light Emitters

- Use several dopants to achieve high efficiency via energy transfer to radiative triplet states
- Mix several dopants to attain
  - ✓ CIE chromaticity coordinates of (0.33,0.33)
  - ✓ High color rendering index Scale of 0-100



## Structure of doped OLED



### Challenges for white:-

- Avoid cascade of energy from blue and green emitters to red emitter
- Tuning device color

University

## Separating dopants into bands

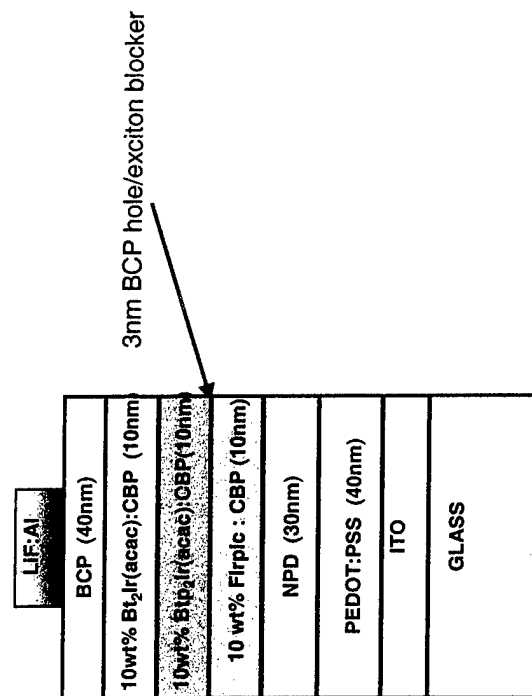
- Prevent energy transfer between dopants.
- Control relative emission intensity of dopants by:
  - ✓ Varying doping concentrations (>1wt%) using thermal evaporation
  - ✓ Adjusting the thickness of bands
  - ✓ Inserting blocking layers
  - ✓ Adjusting the position of the dopants relative to the HTL

### Why does it work?

- Triplets can diffuse much further than singlets (measured ~1000Å)
- Good control over diffusion of excitons using blocking layers and layer thickness

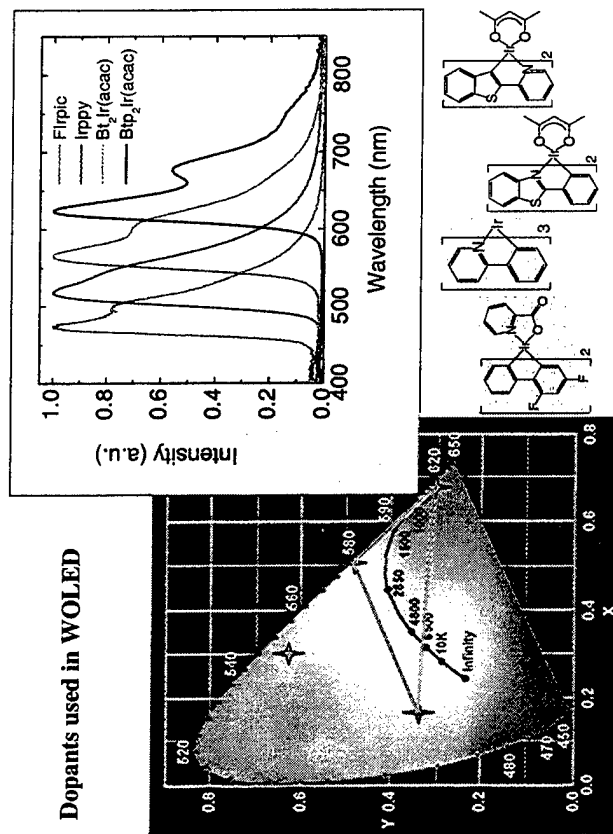
University

## Efficient, Color Balanced White Light Emitter



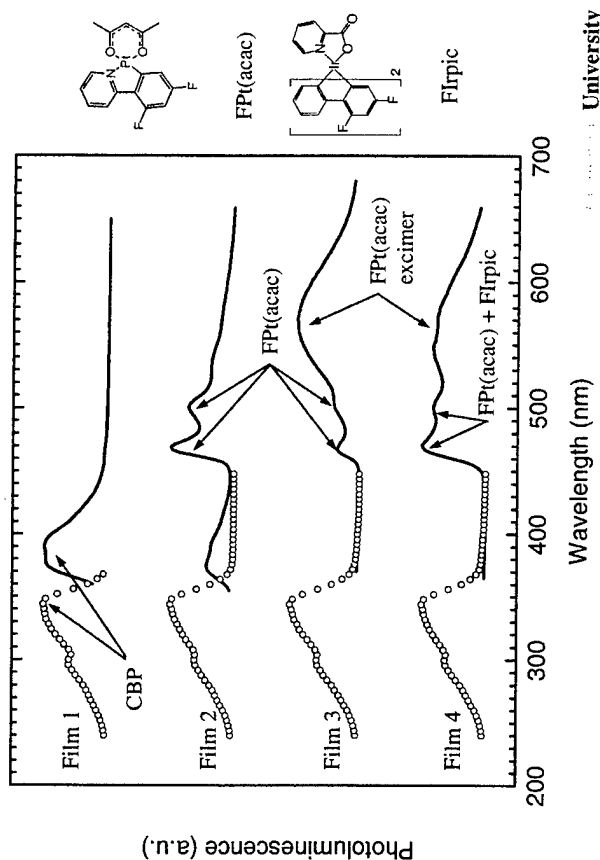
University

## Dopants used in WOLED



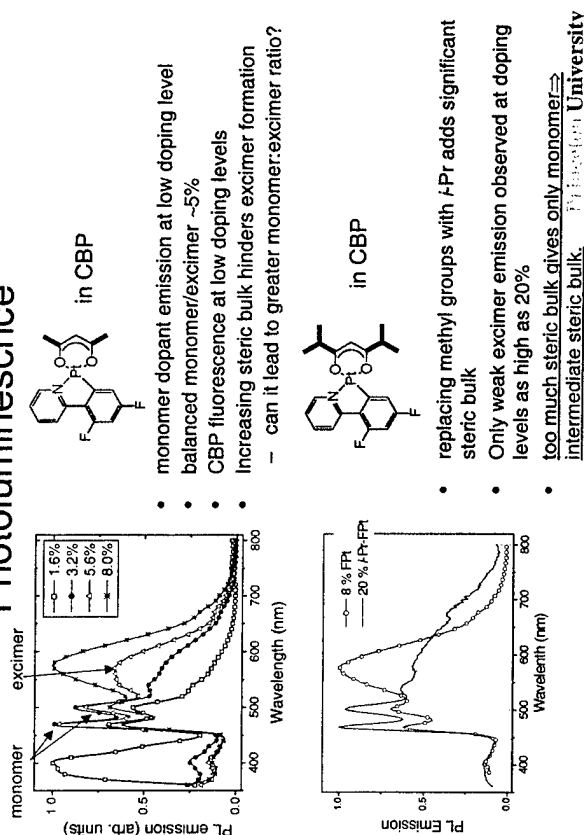
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# Broad Excimer Emission Simplifies Device Structure

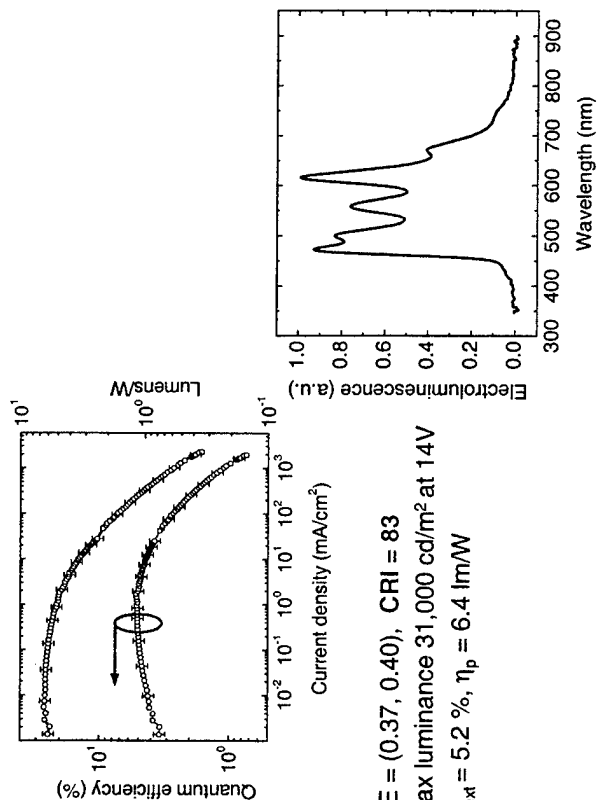


University

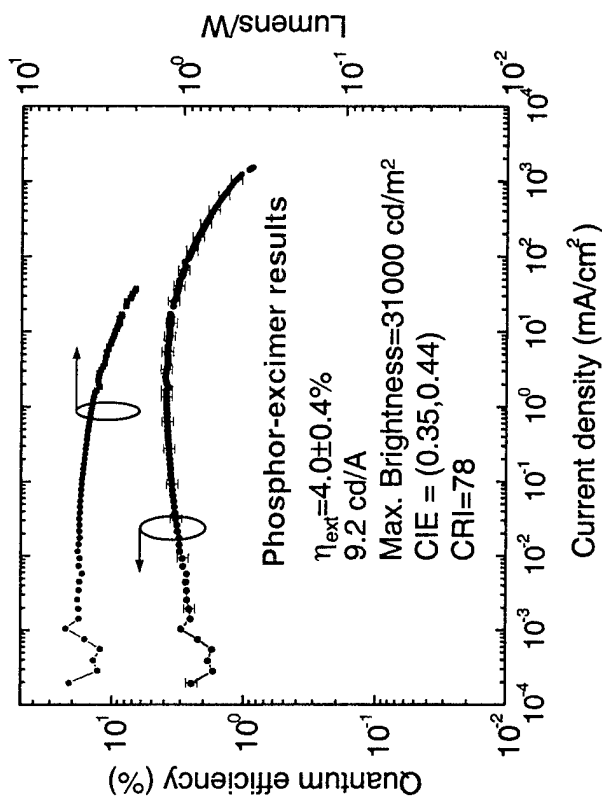
## Single Dopant Monomer – Excimer Photoluminescence



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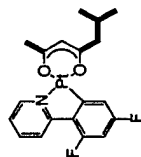


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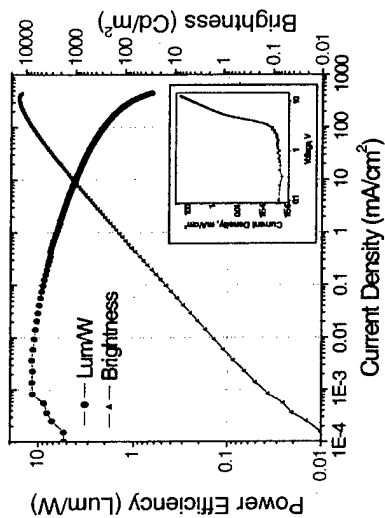
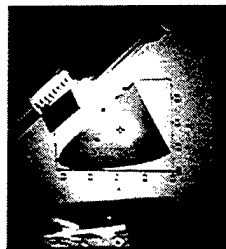
# High Efficiency Single Dopant WOLEDs



doped luminescent layer

CIE: 0.39 0.41

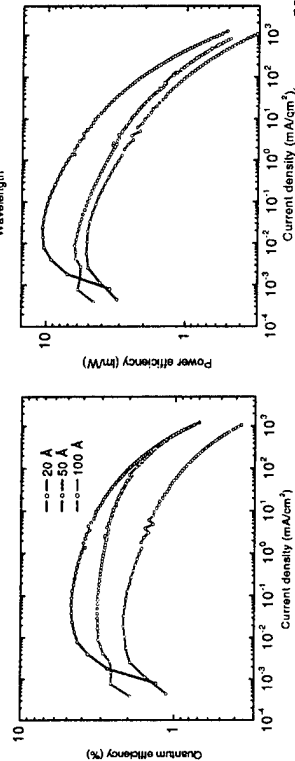
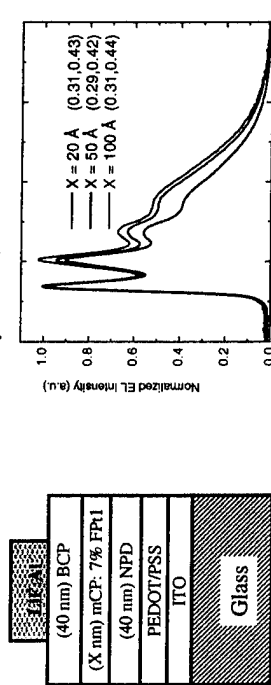
CRI: 76



- Q.E = 5.8% , 9 lm/W @ 50 cd/m²
- Q.E = 4.5% , 5.1 lm/W @ 500 cd/m²

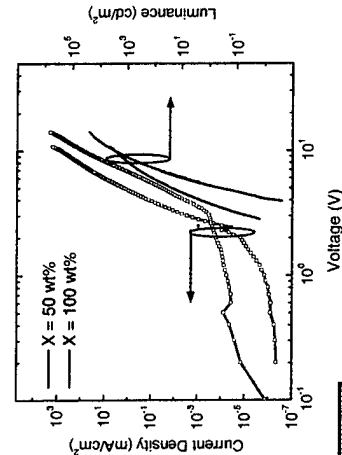
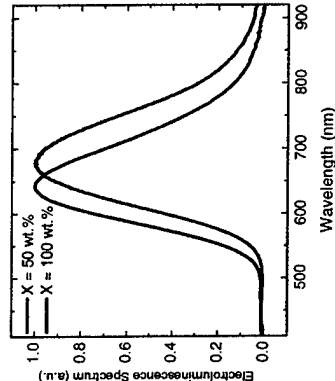
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## White electroluminescence spectra, J-V and luminance

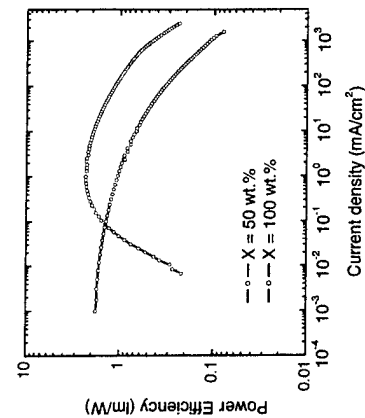
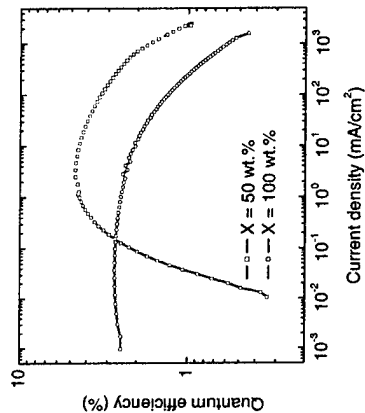


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## Red electroluminescence spectra, J-V and luminance



## Red external power and quantum efficiencies



University

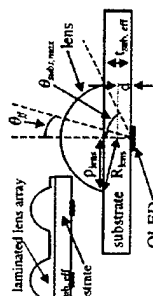
University

## Low index substrates



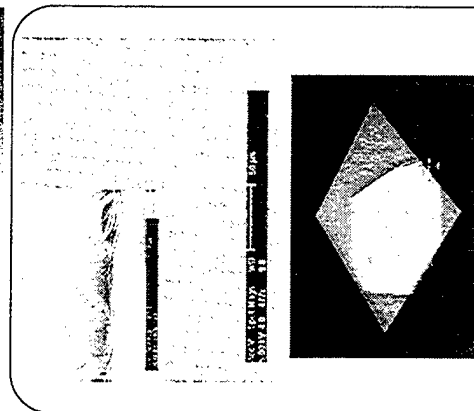
T. Tsutsui, M. Yahiro, H. Yokogawa, K. Kawano, and M. Yokoyama, *Adv. Mater.* **13**, 1149 (2001).

## Lenses



V. Bulovic, V. B. Khalifa, G. Gu, P. E. Burrows, D. Z. Garbuzov, and S. R. Forrest, *Phys. Rev. B* **58**, 3730 (1998).  
 Pictures: C. F. Madigan, M. H. Lu, and J. C. Sturm, *Appl. Phys. Lett.* **76**, 1650 (2000).

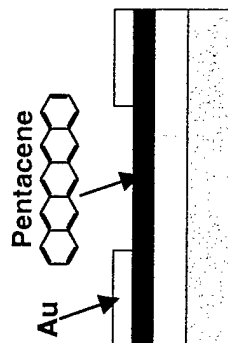
## Optical elements



S. Möller and S. R. Forrest, *MRS Fall Mtg.*, (2001), Paper BB6.9

University

## Thin Film Transistors with Pentacene Channels



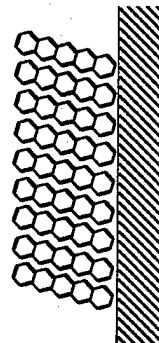
### "Top-contact"

Long (>10μm) channels  
 Shadow Masking /  
 Cold-Welding



### "Bottom-contact"

Shorter channels  
 Photolithography

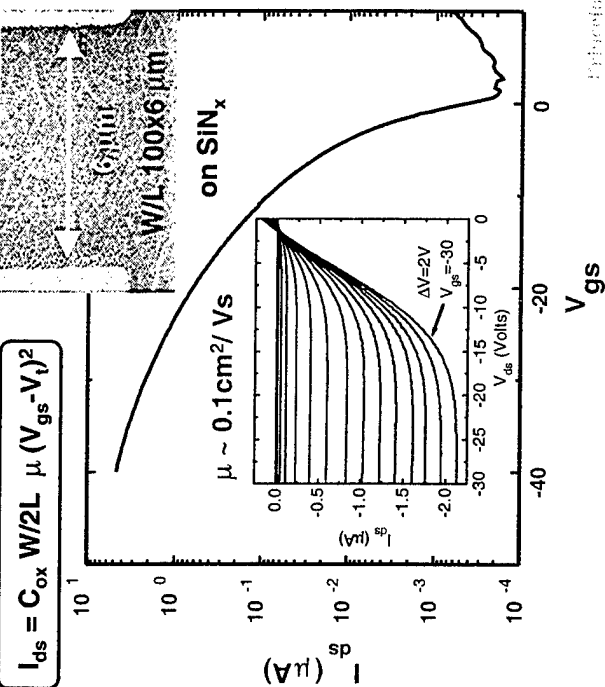


### Charge Transport

Along  $\pi$  overlap  
 Trap-limited

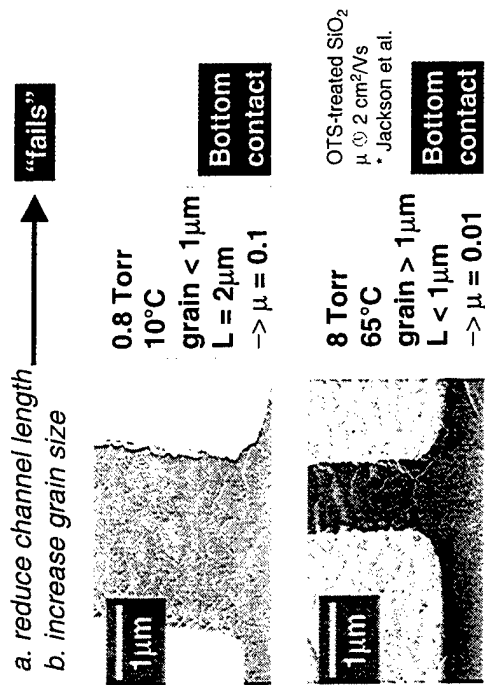
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## Pentacene TFTs by OVPD, Bottom Contact



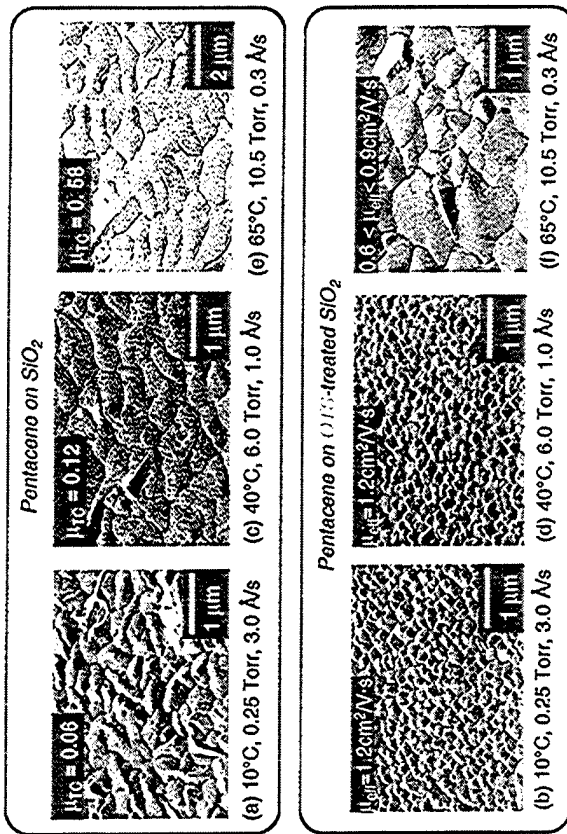
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## Reaching Single-Crystal mobility with BC geometry

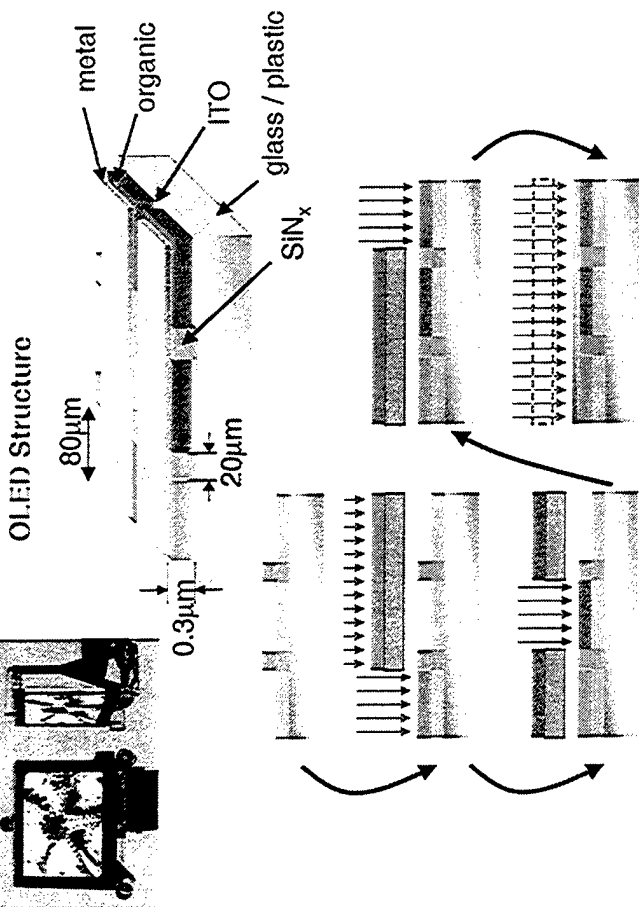


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## Controlling Pentacene Film Morphology - Top Contact Geometry



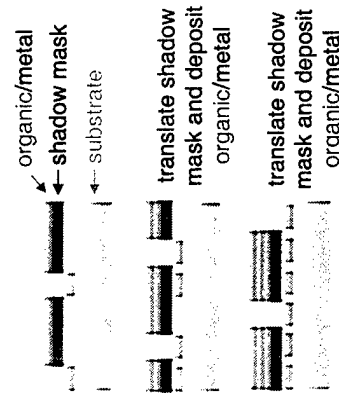
University



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## Patterning of Full Color Displays

- Conventional shadow mask technique



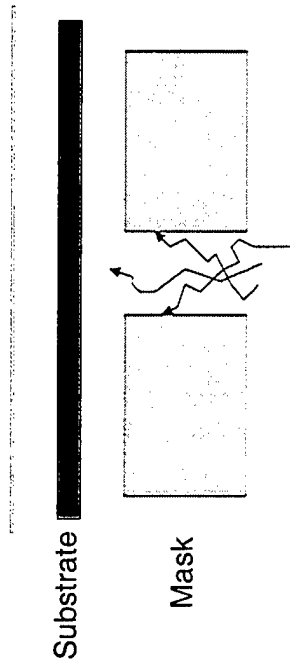
### Limitations:

- Resolution determined by mask thickness
- Requires integrated shadow mask (ISM)
- Requires precise positioning

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# Growth through apertures



- Will surface absorption prevent deposition at the substrate?
- What pattern resolution is achievable?

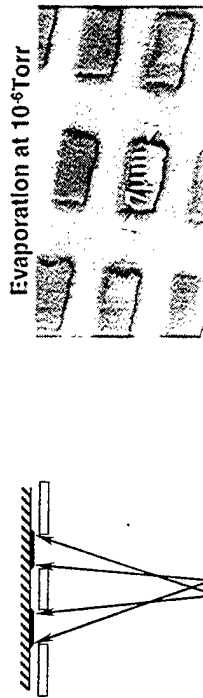
Patterned deposition through masks necessary for full color displays and other applications

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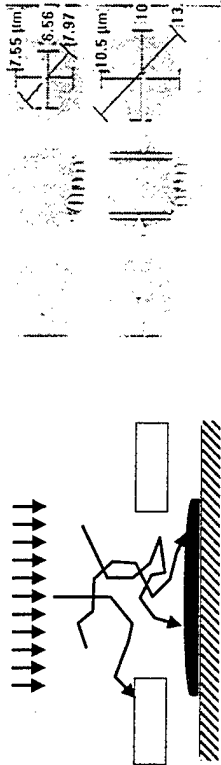
Micropatterning of organic thin films: experiment

Mask thickness =  $7\mu\text{m}$   
Aperture =  $7.5\mu\text{m}$

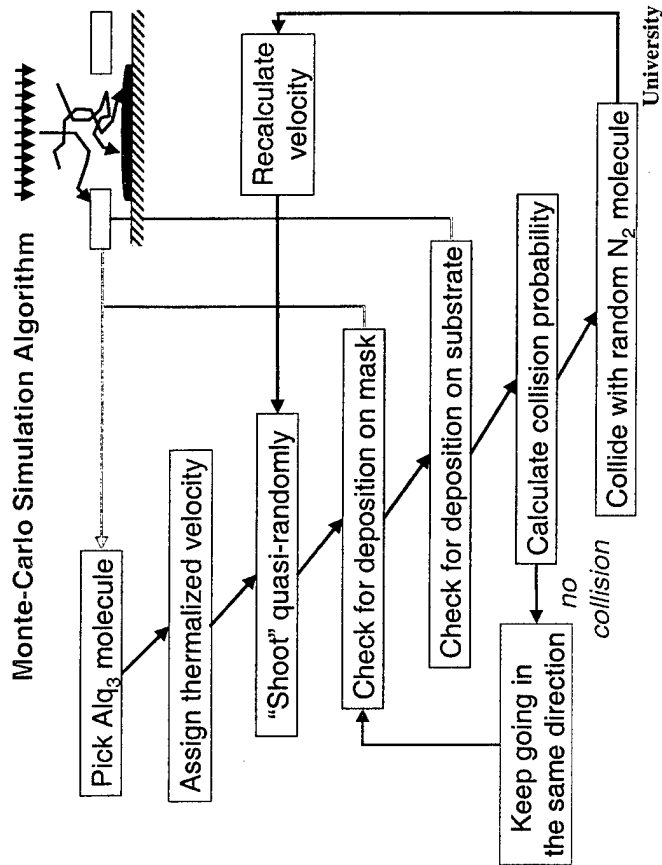
Mask separation  $3\mu\text{m}$   
Carrier velocity  $1\text{ m/s}$



OVPD at  $0.1\text{ Torr}$

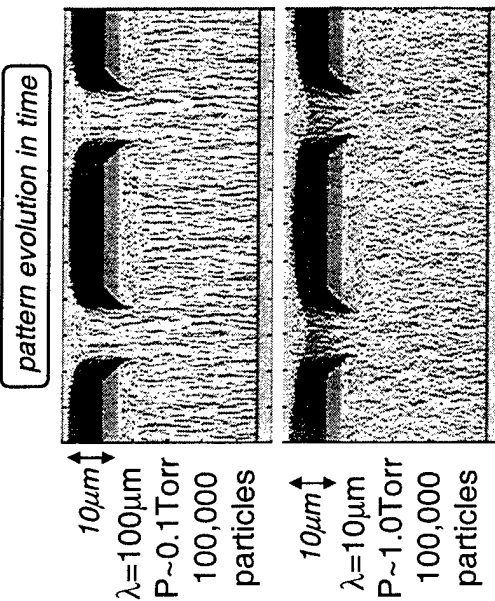


## Monte-Carlo Simulation Algorithm

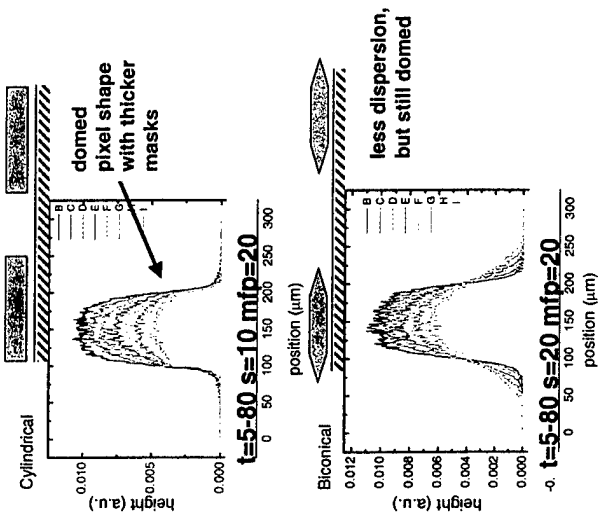


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Alq<sub>3</sub> film deposition in N<sub>2</sub> background



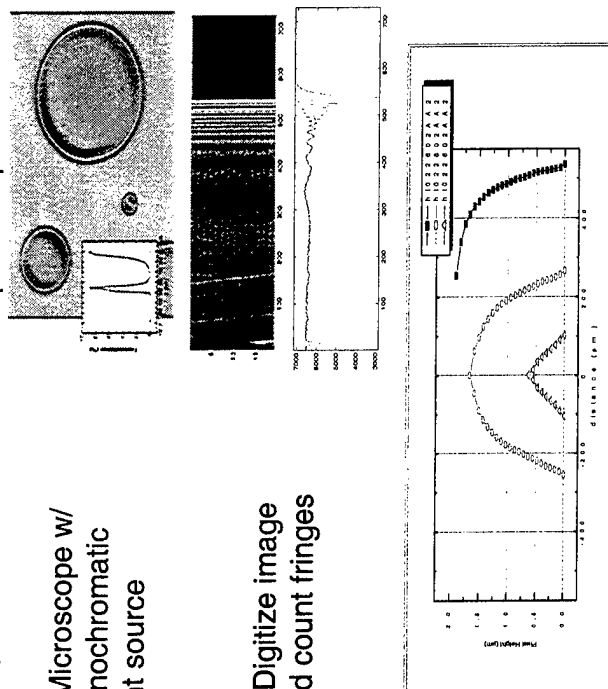
## Effect of masking geometry on pixel shape



University

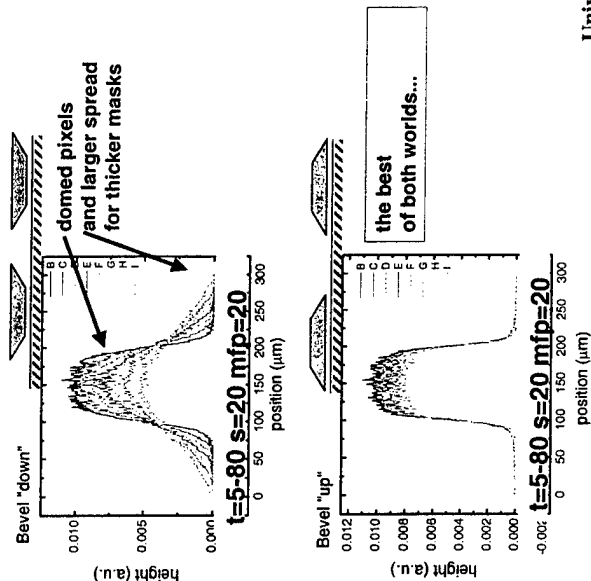
## Experimental determination of pixel shape

1. Microscope w/ monochromatic light source
2. Digitize image and count fringes



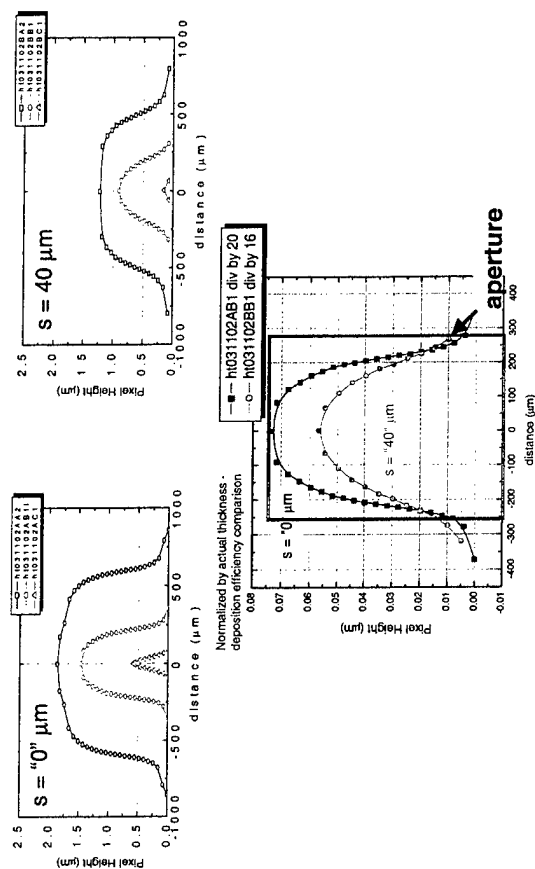
University

## Effect of masking geometry on pixel shape



University

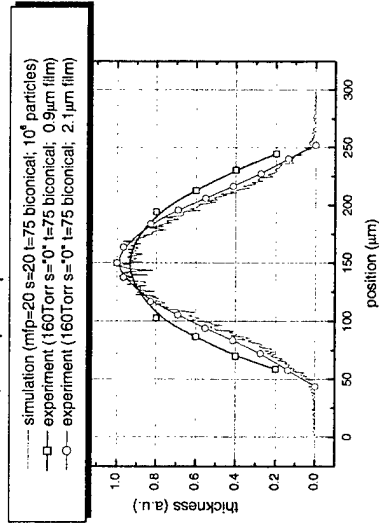
## Example: cylindrical aperture, 0.16 Torr vary pixel size, vary separation



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# Smaller patterns & comparison w/ simulation

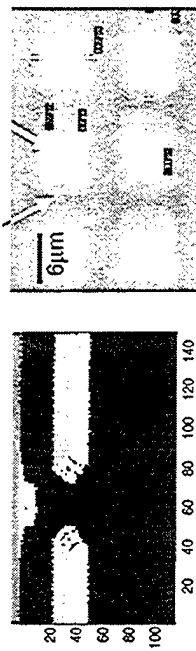
Biconical Mask, 100µm aperture



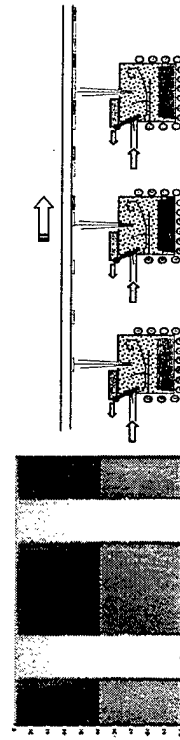
University

# Hybrid OVPD + vacuum Deposition

$\lambda=5\mu\text{m}$  OVPD @ 1 Torr VTE @ 10<sup>-6</sup>Torr



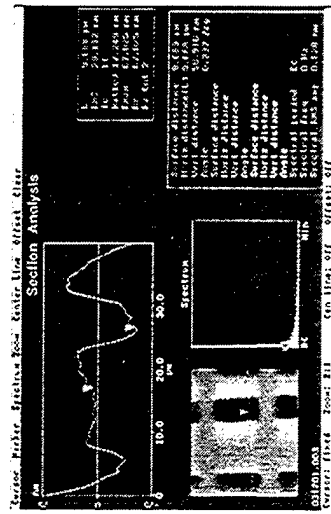
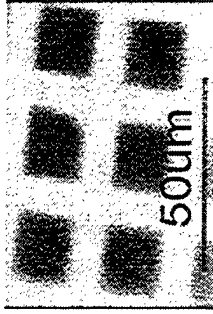
# Organic vapor jet deposition: for home office?



University

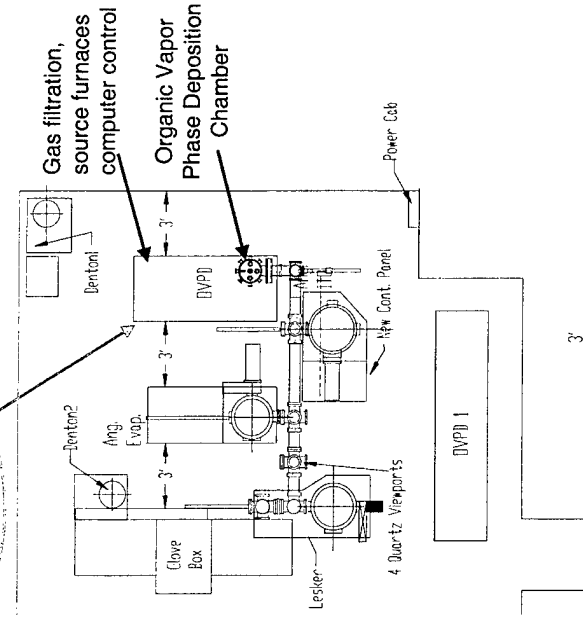
# Really small patterns → AFM

@ 1.4Torr



University

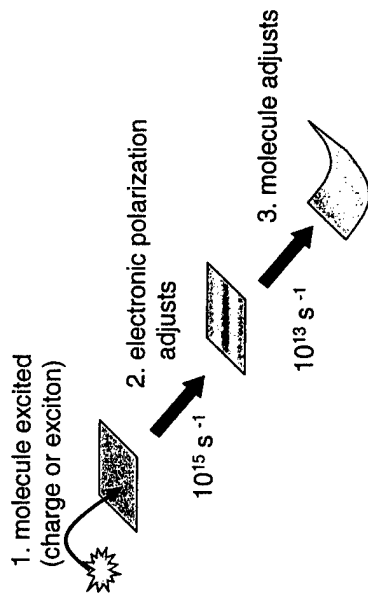
# Full lab layout with new OVPD system



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## INTRODUCTION TO ELECTRON TRANSFER

### Incoherent energy transfer



Born-Oppenheimer approximation:

*electronic motion is much faster than nuclear motion.*

Rate of energy and charge transfer is limited by nuclear motion, and the reconfiguration of the molecules

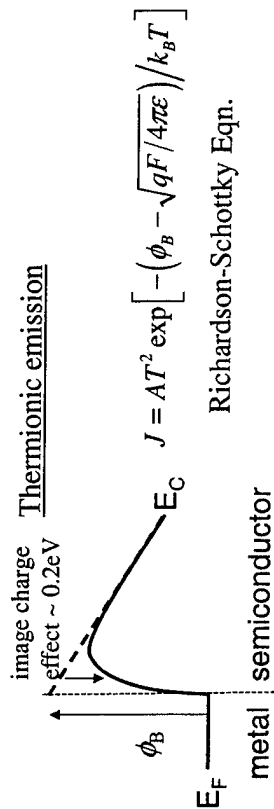
sity

## INJECTION LIMITED MODELS

Thickness dependence of transport in  $\text{Alq}_3$  is injection limited for thin films ( $d < 2000 \text{ \AA}$ ).

Traditionally semiconductor injection is analyzed following thermionic injection or tunneling injection.

Injection is strongly temperature dependent: eliminating tunneling injection.



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## Marcus electron transfer

Represent molecules as simple harmonic oscillators.  
Intermolecular overlap energy is small  $\sim 10 \text{ meV}$ .

Both molecules in relaxed state:



Reorganizational energy required  $= \lambda$

If both molecules adjust:



Reorganizational energy required  $= \lambda/4$

Typically,  $\lambda \sim 0.1 - 0.5 \text{ eV}$ .

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## PROBLEMS WITH THERMIONIC EMISSION

Examine different cathodes

on  $\text{Alq}_3$ .

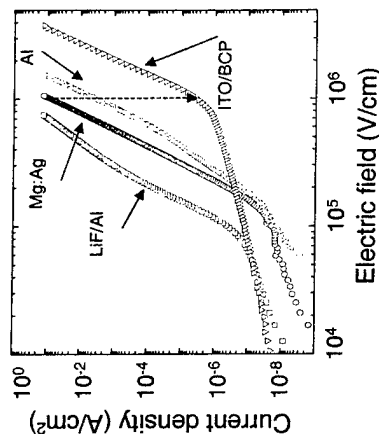


Work functions:

Mg:  $3.7 \text{ eV}$

Al:  $4.0 \text{ eV}$

Indium tin oxide (ITO):  $4.7 \text{ eV}$



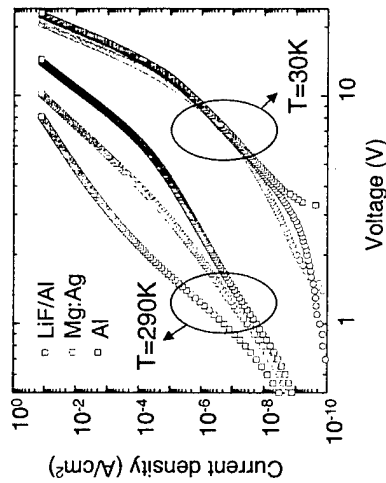
From work function alone, we expect  $1 \text{ eV}$  difference between Mg and ITO to reduce injection by factor of  $10^{18}$ , actually only  $10^5$ .

L.S. Hung et al. Appl. Phys. Lett. 70, 152, 1997

G. Parthasarathy et al. Appl. Phys. Lett. 76, 2128, 2000

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## NO CATHODE DEPENDENCE AT LOW TEMPERATURES



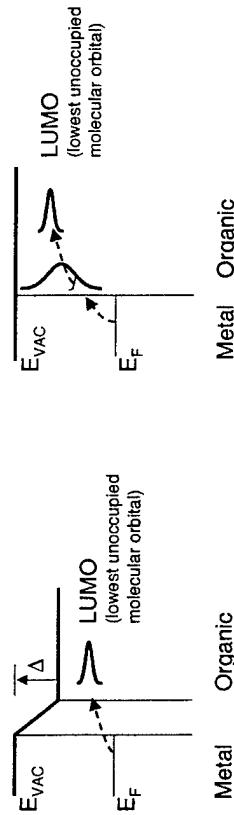
Transport is injection limited for  $T < 300\text{K}$ .

But transport is independent of cathode at low temperature - injection must depend on interfacial organic layers.

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## THE METAL/ORGANIC INTERFACE

Reasons why the metal work function may not be an accurate measure of cathode injection efficiency.



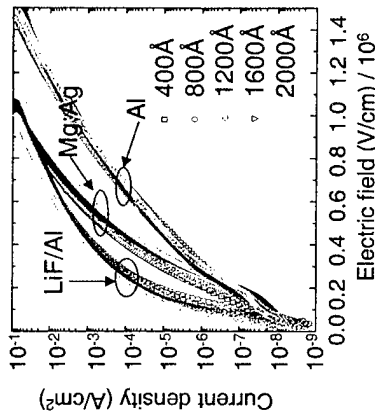
An interfacial dipole may shift the surface energy of the organic film

Intermediate states may reduce the overall hopping barrier

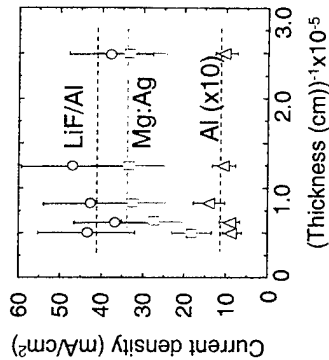
The presence of an interfacial dipole induces the intermediate states

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## THICKNESS DEPENDENCE (II)



Thickness dependence at  $F = 0.9 \times 10^6 \text{ V/cm}$



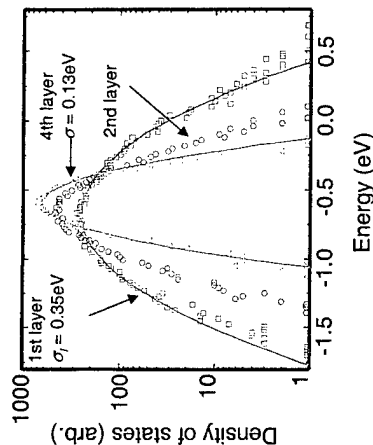
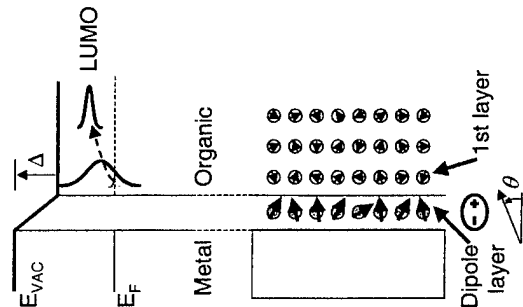
If transport is space charge limited (bulk limited),  $J \sim 1/d$ , irrespective of field dependence of mobility.

Characteristics are consistent with injection-limited transport.

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## DISORDER IN THE INTERFACIAL DIPOLE

Assuming interfacial dipoles of strength  $\sim 30\text{D}$ , and Gaussian orientation disorder with variance  $\sigma = \pi$  radians, we get:



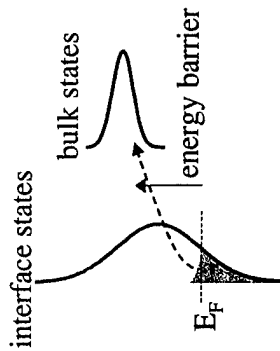
Energy (eV)

Alternately, disorder may be due to local variation in magnitude of dipoles

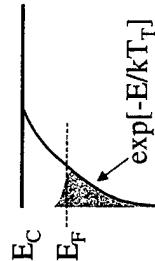
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## FEATURES OF THE INTERFACIAL STATE MODEL

- Limiting step is hop from organic interface to organic bulk
- Transport can be explained using only intrinsic properties  
No need for extrinsic effects such as traps.
- Broad distribution of interface states generates power law transport -similar to trapped charge limited transport (distribution of states below a conduction level)

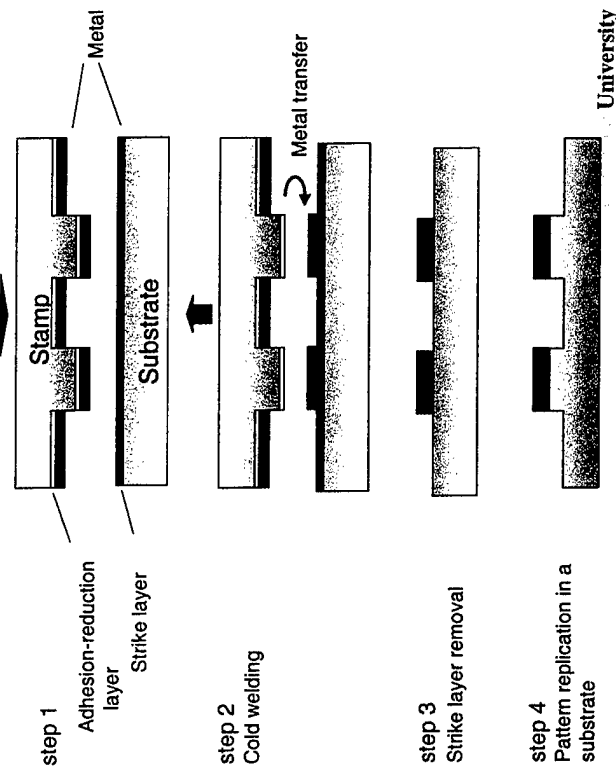


Classical trap charge limited conduction



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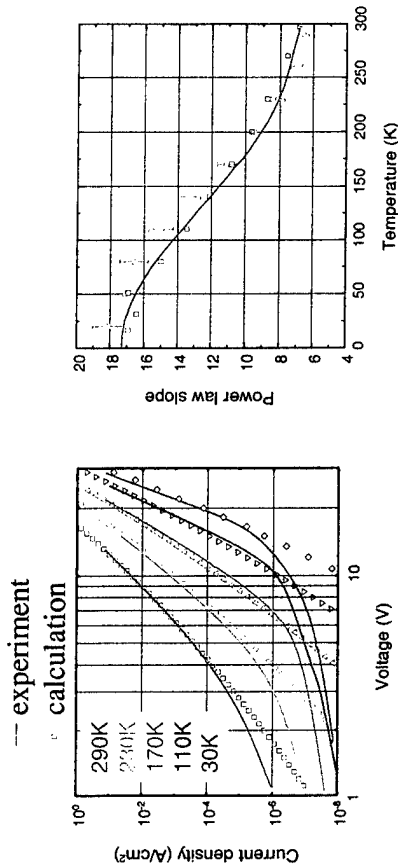
## Additive Cold-welding Process



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## TEMPERATURE DEPENDENCE OF Mg:Ag/Alq<sub>3</sub> INTERFACE

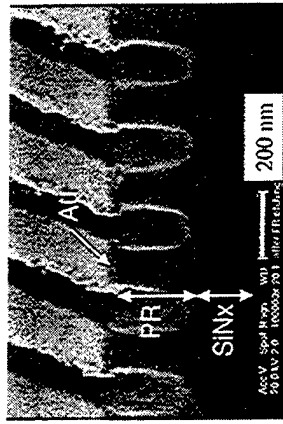
Device: 300 Å Ag / 1000 Å 25:1 Mg:Ag / 1200 Å Alq<sub>3</sub> / 1000 Å Mg:Ag / SiN<sub>x</sub> / Si



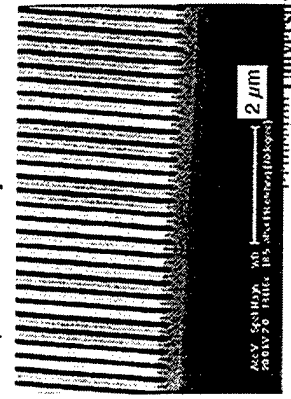
Fit using polaron model for interfacial hop:  
includes temperature dependence of phonon distribution

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## Cold-welding for high resolution lithography



photoresist layer is etched

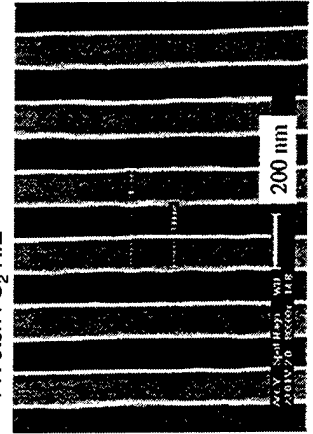


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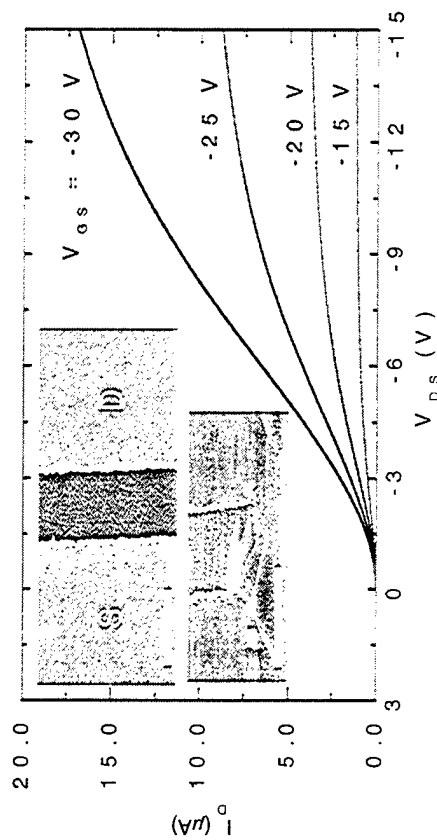
substrate: Si/SiN<sub>x</sub>/PR/  
stamp: Si/Alq<sub>3</sub>/

200 MPa, 10 MPa/s, no hold time.  
Au etch : Ar sputtering  
PR etch : O<sub>2</sub> RIE



transferred metal lines

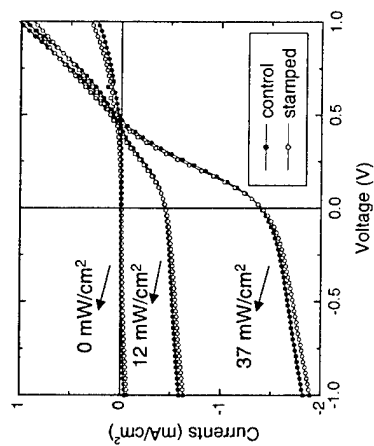
## Additive Cold-welding for Narrow Gate OTFTs



$L=1\ \mu\text{m}$   
 $\mu\sim 0.1\ \text{cm}^2/\text{V}\cdot\text{s}$

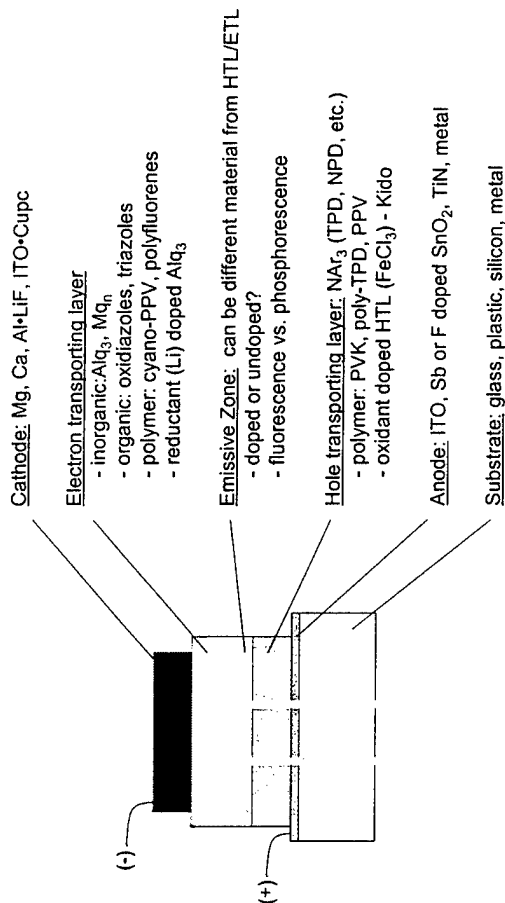
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## Additive Cold-welding for Organic Solar Cells



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## Heterostructure OLEDs





































































































































































































































# Advances in Chemistry of Materials for OLEDs

Mark Thompson  
USC

Library of diamnes

Library of dyes

$$\left\{ \begin{array}{l} T_m \\ E_g^m \\ PL(\lambda_{max}) \\ abs(\lambda_{max}) \end{array} \right\}$$

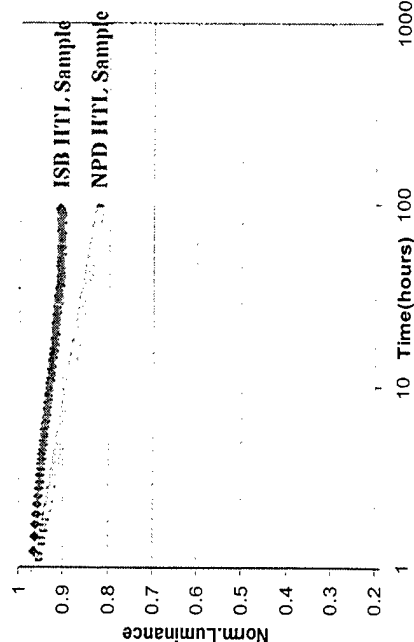
						
						
						
						
						
						
						
						
						
						
						
						
						
						
						
						
						
						
						
						
						
						
						
						
						
						
						
						
						
						
						
						
						

- Device structure: ITO/HTL (400 Å)/Alq3 (400 Å)/Mg-Ag
- ISB has the best combination of efficiency and low voltage operation (similar to NPD), highest  $T_g$
- D. F. O'Brien, et. al., *Advanced Materials*, **1998**, 10, 1108-1112.



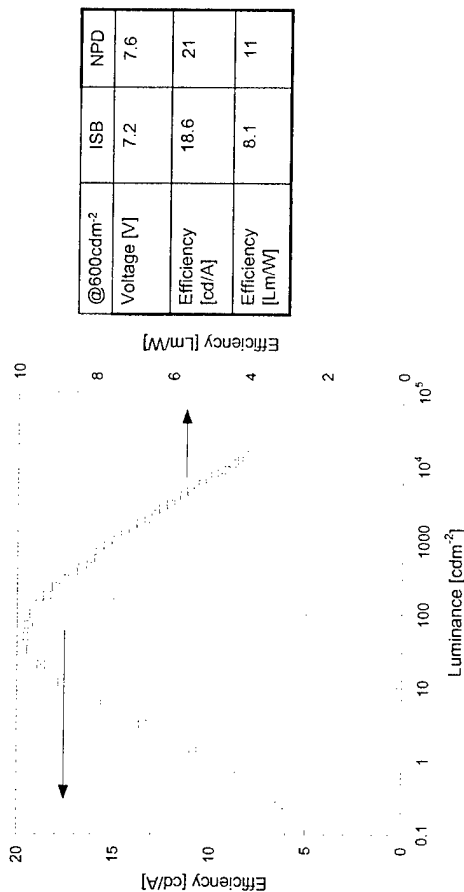
## High T<sub>g</sub> HTL Lifetime Comparison

ITO/CuPc(100A)/HTL(500A)/CBP:PtOEP(300A)/Alq<sub>3</sub>(200A)/MgAg



UNIVERSAL DISPLAY CORPORATION

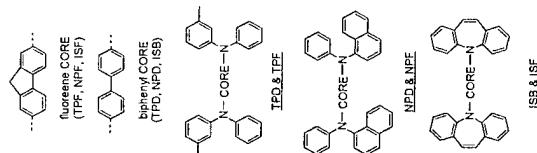
## G1 structure with ISB as a HTL Efficiency vs. luminance



UNIVERSAL DISPLAY CORPORATION

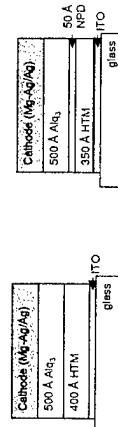
@600cdm <sup>-2</sup>	ISB	NPD
Voltage [V]	7.2	7.6
Efficiency [cd/A]	18.6	21
Efficiency [lm/W]	8.1	11

## Fluorene Cored HTLs



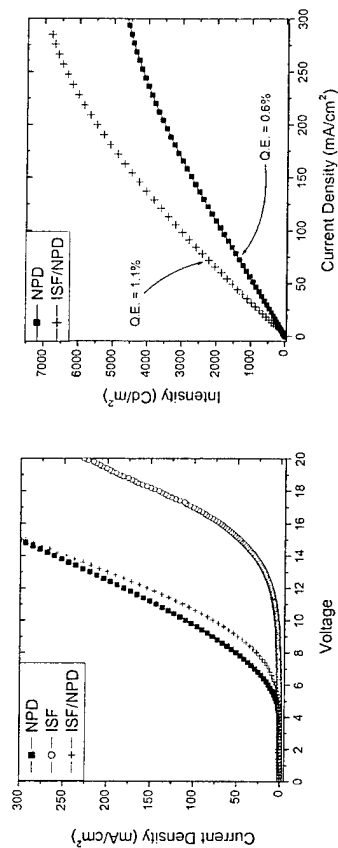
Material Acronym	TPF	TPD	NPF	NPD	ISF	ISB
T <sub>g</sub> (°C)	78	60	118	95	161	115
1 <sup>st</sup> Oxidation (vs. Ag/AgCl)*	0.626	0.733	0.658	0.767	0.516	0.699
Absorption/Emission (nm)	340/398	315, 355/396	360/470	270, 340/450	295/530	300/530

- Fluorene core gives higher T<sub>g</sub> than biphenyl
- Lowers oxidation potential: raises HOMO energy
- What about OLEDs?



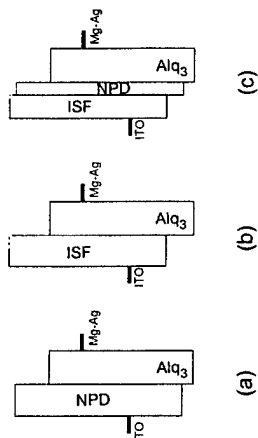
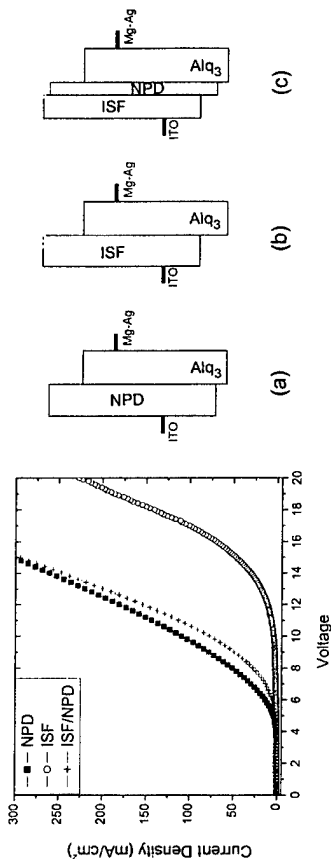
D. Loy, *et. al.*, *Adv. Func. Mat.*, 2002, 12, 245.

## ISF based OLEDs



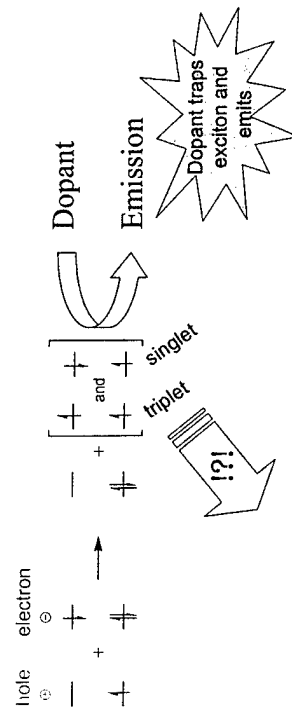
- NO LIGHT for ISF/Alq<sub>3</sub> device
- NPD interface layer is needed to efficiently inject holes from ISF to Alq<sub>3</sub>
- ISF HOMO is too shallow

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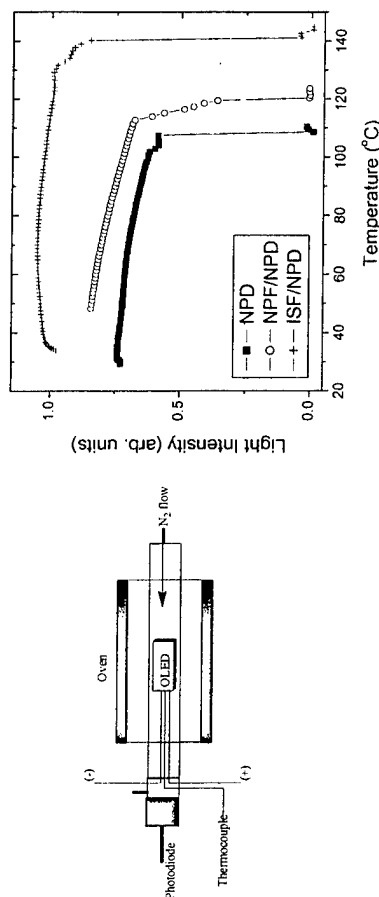
## Hole/electron recombination leads to singlet and triplet excitons



- Expected singlet fraction based on simple spin statistics = 25%
- Energy transfers from host/matrix excitonic states to dopant conserve spin.
- Phosphorescence (triplet emission) is formally a forbidden process.

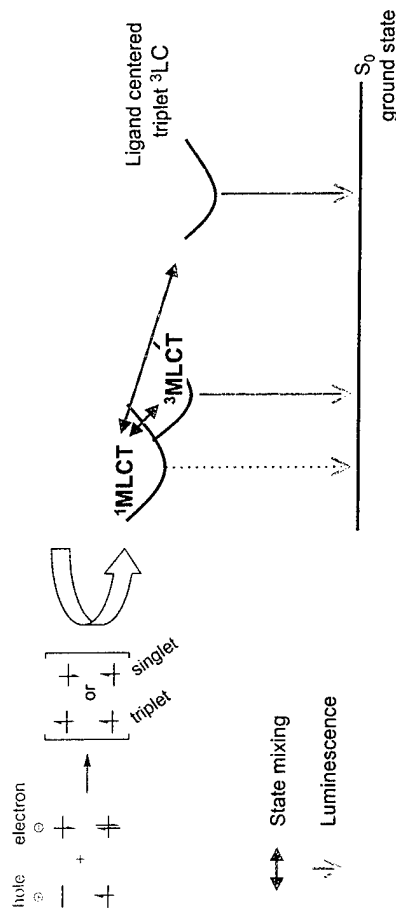
Experimentally determined singlet fraction for Alq<sub>3</sub> based OLEDs = 22±3%  
M.A. Baldo, et al., Phys. Rev. B (1999)

## Thermal Stabilities



- ISF/NPD HTL crashes 45°C above the NPD T<sub>g</sub>
- Low T<sub>g</sub> interface layer is not a problem!

## Heavy metal facilitated triplet emission



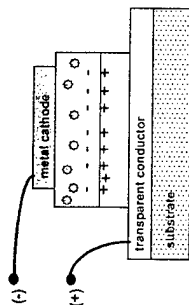
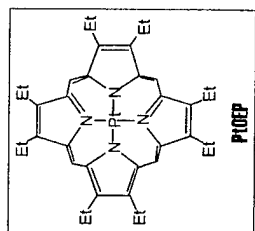
- Strong spin-orbit-coupling mixes singlet and triplet MLCT states, for M = Ir, Pt, Os, Re, etc.
- Mixing of triplet states with <sup>1</sup>MLCT makes phosphorescence a largely allowed transition, short triplet lifetime

## Pt based phosphorescent dye/dopant

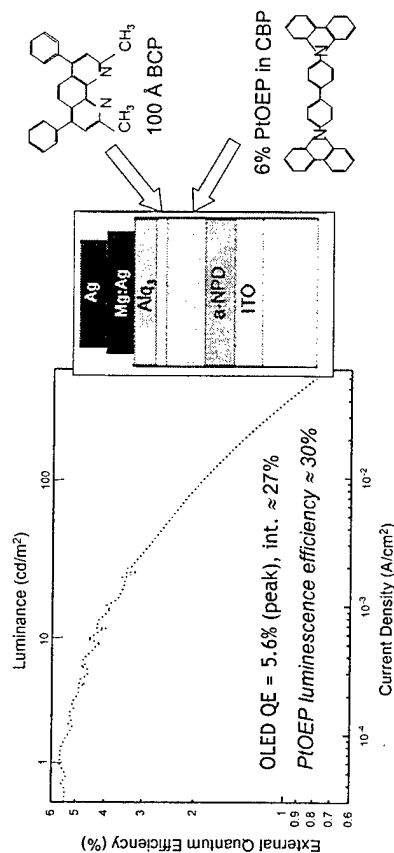
- Platinum octaethylporphine (PtOEP) has high phosphorescence quantum efficiency\*
  - PL efficiency (phosphorescence) is 0.5 at 298 K (in polystyrene),  $\tau = 91$  msec
  - PL efficiency 0.9 at 77K,  $\tau = 130$  msec
- Simple, two layer structure gives good eff.
  - 4 % external at low brightness
  - Exclusive PtOEP triplet emission.

See: M.A. Baldo, et. al., *Nature* (1998)

- G. Ponterini, et al., *J. Am. Chem. Soc.*, (1983)
- D.B. Papkovski, *Sens. Actuators*, (1995)
- J. Rodriguez, et al., *Chem. Phys. Lett.*, (1988)



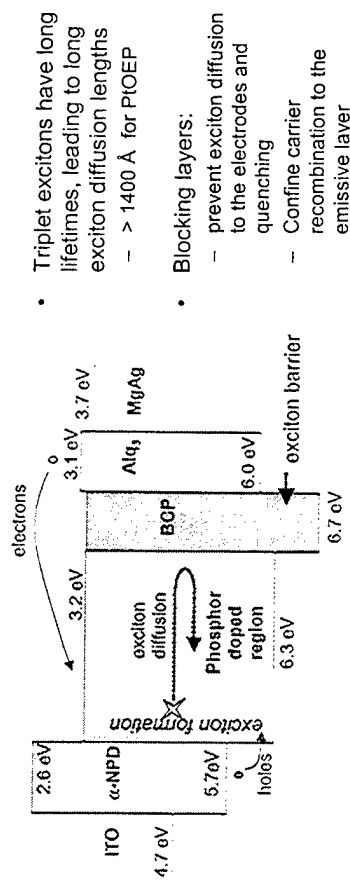
## Quantum Efficiencies of PtOEP OLEDs with an Exciton Blocking Layer



- Q.E. decay as current is increased is due to T-T annihilation
  - $T_1 + T_1 \rightarrow S_0 + S_1$ , second order quenching process !!
  - decrease the effects of T-T annihilation by:
    - decrease [triplets], lower the doping level: phosphor saturation a problem
    - short triplet lifetime will decrease T-T annihilation

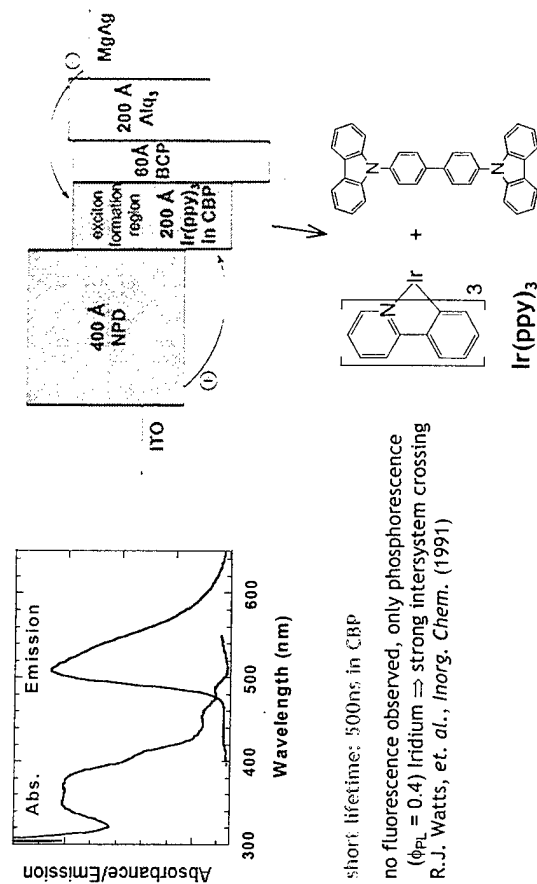
See: D. O'Brien, et al., *Appl. Phys. Lett.* (1999)

## Efficient electrophosphorescent device structure



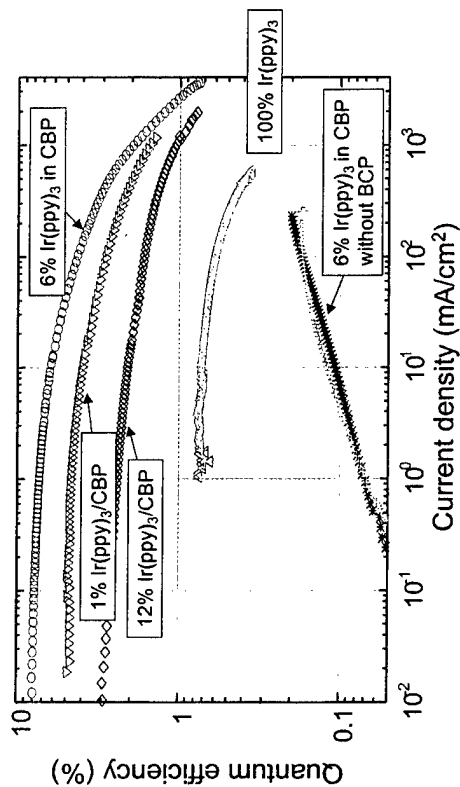
- Triplet excitons have long lifetimes, leading to long exciton diffusion lengths
  - $> 1400$  Å for PtOEP
- Blocking layers:
  - prevent exciton diffusion to the electrodes and quenching
  - Confine carrier recombination to the emissive layer

## Organometallic Ir Phosphor



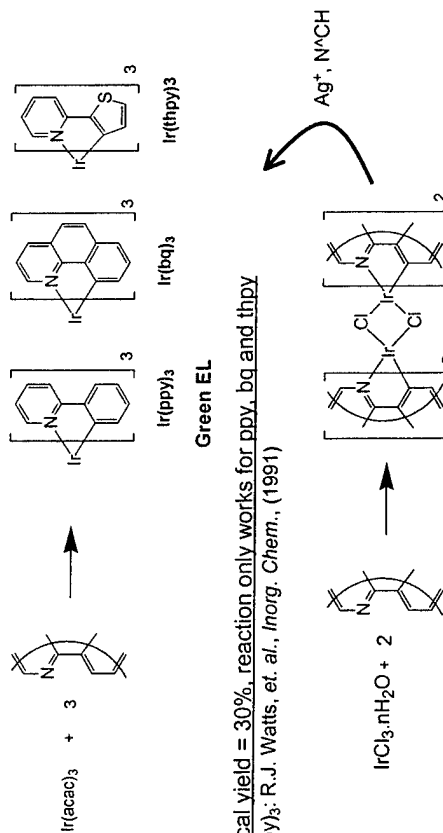
M.A. Baldo, et al., *Appl. Phys. Lett.*, 1999

## External quantum efficiency of Ir(ppy)<sub>3</sub> in CBP



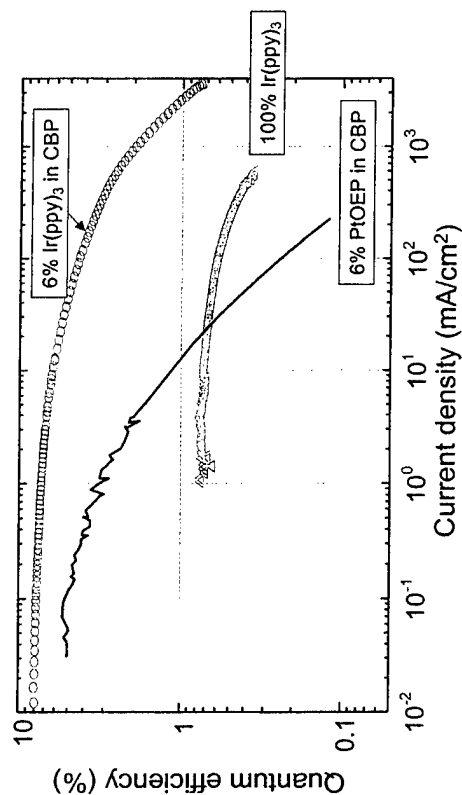
- ca. 1/5 of the light is forward scattered, thus  $\eta(\text{internal}) = 5 \times \eta(\text{external})$   
peak internal efficiency  $\approx 40\%$

## Synthesis of Cyclometallated Ir Complexes



typical yield > 90%, not emissive in solution or solid state  
 M. Nonoyama, *Bull. Chem. Soc. Jpn.* (1974)

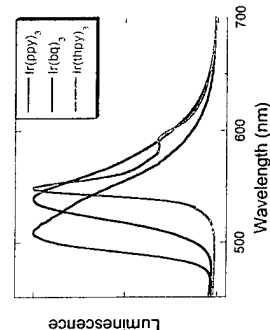
## External quantum efficiency of Ir(ppy)<sub>3</sub> vs. PtOEP in CBP



- PtOEP and Ir(ppy)<sub>3</sub> devices have the same structure.

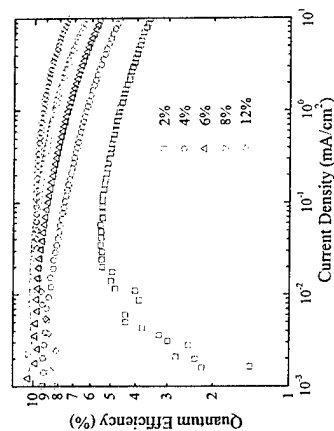
## Electroluminescent Spectra of Cyclometallated Phosphors

- All phosphors have  $\tau < 5 \mu\text{sec}$
- Spectra constant on increasing bias/current



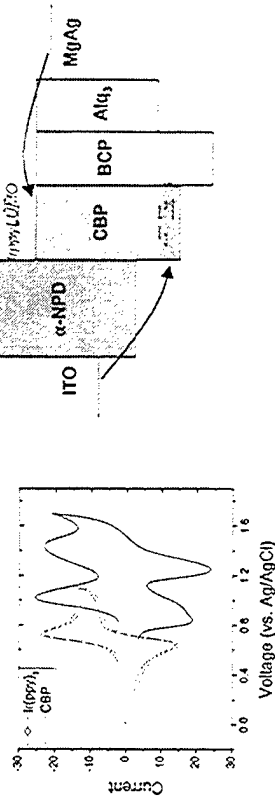
Dopant	peak $\eta_{\text{ext}}$ (%)
Ir(bq) <sub>3</sub>	10
Ir(thpy) <sub>3</sub>	4 (unoptimized)

CBP:Ir(bq)<sub>3</sub> With BCP Cap



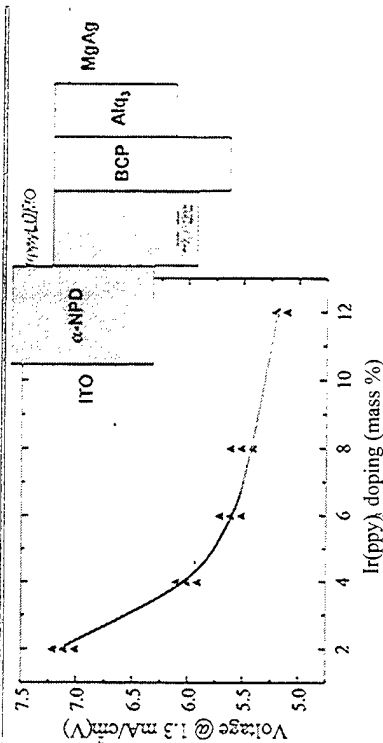
## Ir(ppy)<sub>3</sub> traps holes in CBP

Cyclic voltammograms of Ir(ppy)<sub>3</sub> and CBP



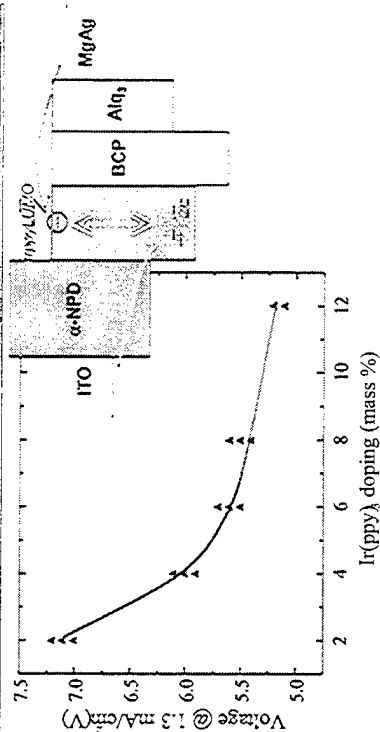
- Ir(ppy)<sub>3</sub> HOMO is 300 mV above the CBP HOMO
  - Same picture from both UPS and electrochemical measurements
- Ir(ppy)<sub>3</sub> reduction is 3 V above oxidation, i.e. Ir(ppy)<sub>3</sub> LUMO is above CBP
  - Y. Oshawa, et al., *J. Phys. Chem.*, 1987
  - Carrier gap (oxid. – red.) matches the <sup>1</sup>MLCT energy

## Conduction through Ir(ppy)<sub>3</sub> “trap” states



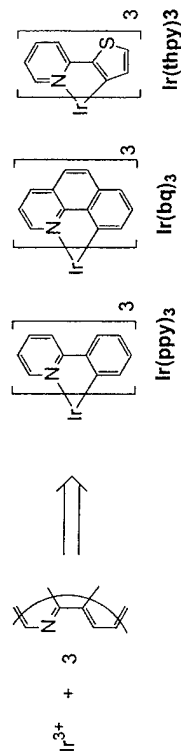
- Holes are carried by the Ir(ppy)<sub>3</sub> dopant at doping levels > 5%
- Hole leakage into Alq<sub>3</sub> will be dominant without hole blocker (BCP)
- All holes are localized on dopants, hole-electron recombination at the dopant
- Same Behavior is observed for other Ir based dopants (Ir(bq)<sub>3</sub> and ppy<sub>2</sub>Ir(acac))

## Conduction through Ir(ppy)<sub>3</sub> “trap” states

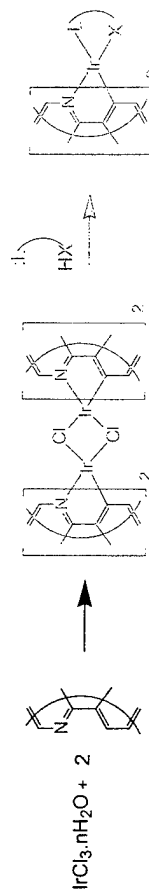


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## Synthesis of Cyclometallated Ir Complexes

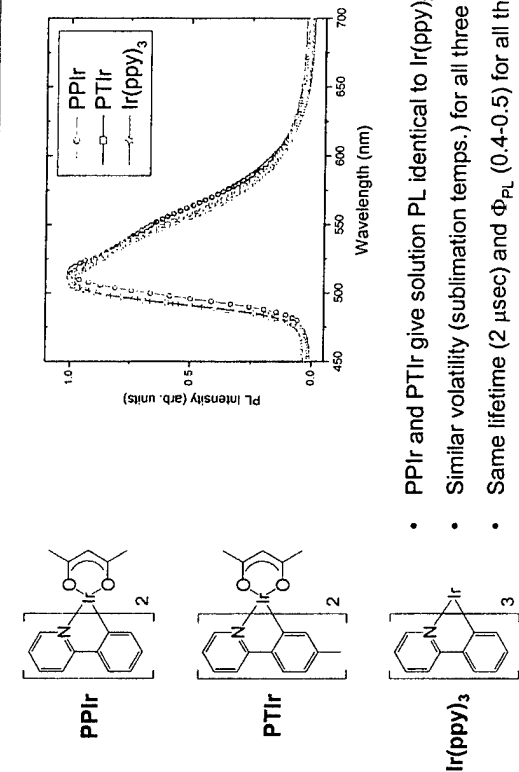


Reactions only work for ppy, bq and thpy ligands (and substituted derivatives)



typical yield > 90%, similar yields for a wide variety of ligands  
1<sup>st</sup> step: M. Nonoyama, *Bull. Chem. Soc. Jpn.* (1974)

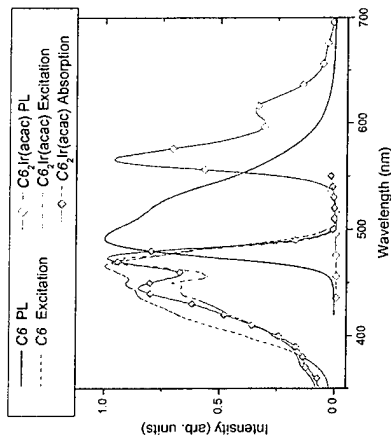
## PL spectra of PPIr and PTIr



All acac cpds. emit with  $\mu$ sec lifetimes and  $\phi_{PL} = 0.2-0.7$

S. Lamansky, et. al., *J. Am. Chem. Soc.* (2001)

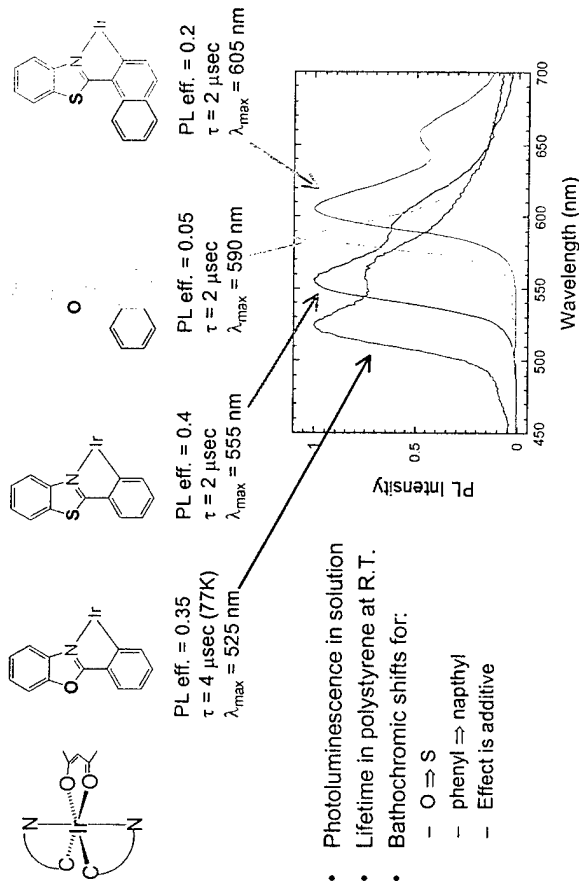
## MLCT vs. LC excited states



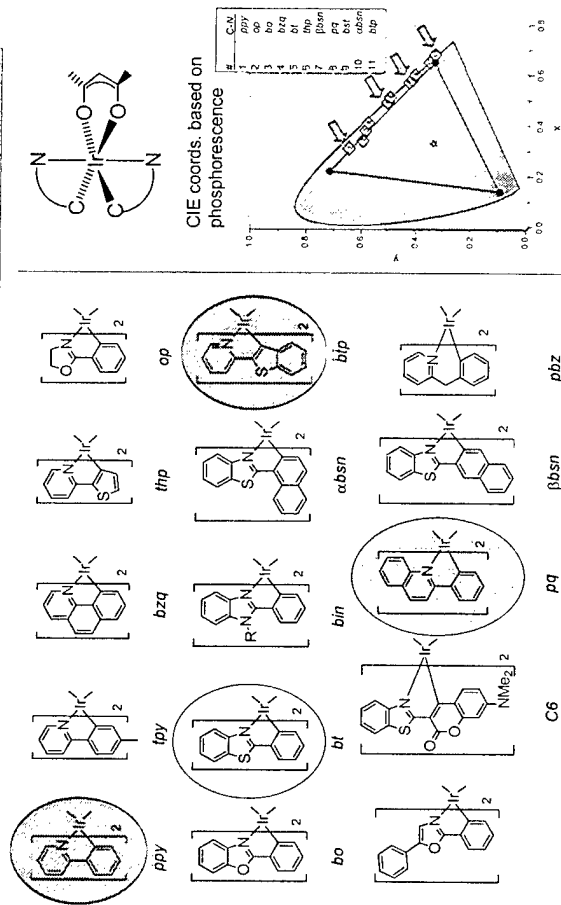
- Coumarin 6 (C6) is a common green laser dye, used to fabricate green fluorescent OLEDs

- MLCT energy similar for *ppy*, *thp*, *btp* (450-475 nm).
  - The choice of  $^3\text{MLCT}$  or  $^3\text{LC}$  emitting state depends on which is lower in energy
  - Small Stokes shift is expected for MLCT emission.
- When this complex is cyclometallated to Ir the emission shifts to orange
    - Ir shifts dominant emission process to C6 based phosphorescence
    - Excitation spectra of  $\text{C6}_2\text{Ir}(\text{acac})$  show lines for C6 as well as MLCT transitions for " $^1\text{L}_2\text{IrX}$ "
    - $\eta$  (PL) for  $\text{C6}_2\text{Ir}(\text{acac}) = 0.6$  and  $\tau = 14 \mu\text{sec}$

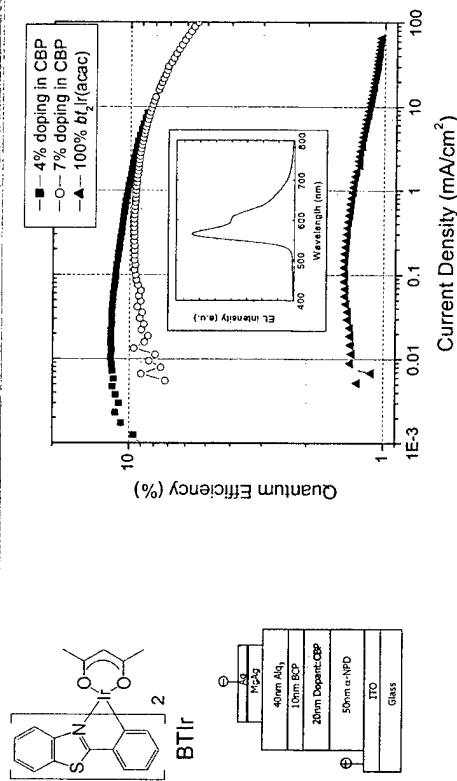
## Ligand Effects on Emission energy



## Green, yellow and red phosphors for OLED study



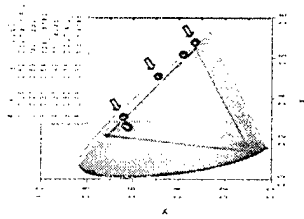
## Performance of BTIr doped OLED (yellow emission)



- Peak external quantum Efficiency = 11%
- Efficiency with 100% BTIr emissive layer > 1.5%: very weak self quenching

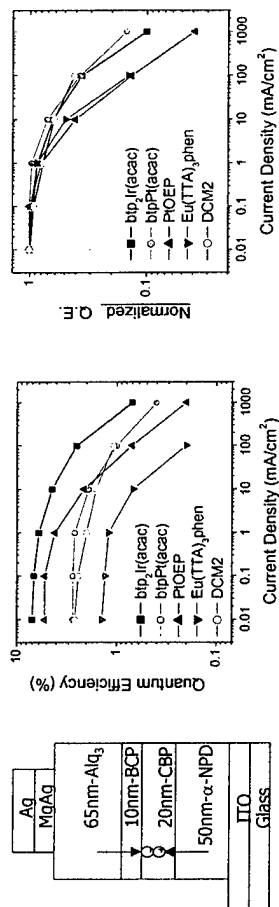
## $(\text{C}^*\text{N})_2\text{Ir}(\text{acac})$ ( $\text{C}^*\text{N}$ = ppy, bt and btp) doped (7%) OLED performance

$\text{C}^*\text{N}$ ligand	ppy	bt	btp
EL color	Green	Yellow	Red
Peak wavelength (nm)	525	565	617
Luminance @ $1 \text{ mA}/\text{cm}^2$ ( $\text{cd}/\text{m}^2$ )	441	300	62
Drive voltage (V) @ $1 \text{ mA}/\text{cm}^2$	7.2	7.3	8.5
Ext. quantum efficiency (%) @ $1 \text{ mA}/\text{cm}^2$	10.0	9.7	6.6
" @ $10 \text{ mA}/\text{cm}^2$	7.6	8.3	6.0
" @ $100 \text{ mA}/\text{cm}^2$	5.4	5.5	4.6
Power efficiency ( $\text{lm}/\text{W}$ ) @ $1 \text{ mA}/\text{cm}^2$	18	11	2.2



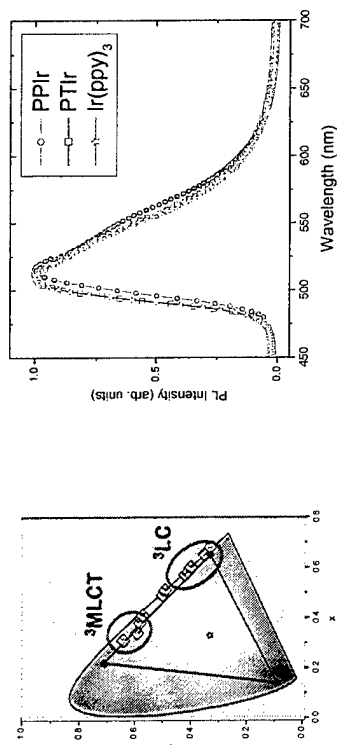
- Similar properties for PQR (orange) OLED
- All dopants give external eff. > 11 % for optimized structures (CBP host)
- Phosphors can be switched in a "modular" fashion with very little alteration of device performance

## Saturated red OLEDs

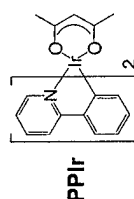


- Doping concentration optimized for each dopant
- DCM2 device is not red, emission is yellow-orange (low doping concentration)
  - Fluorescence based device, NOT phosphorescence
- btp complexes of Ir give the best performance
  - Highest peak efficiency
  - Slowest drop off in eff. as a function of current density

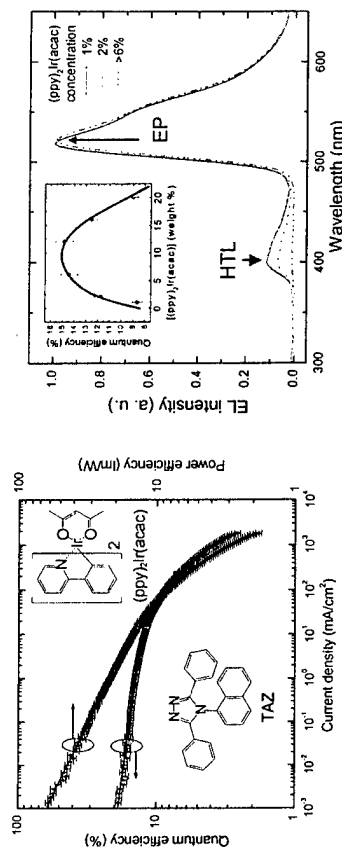
## Green Emission from MLCT States



- Changes in C<sup>N</sup> primarily affect <sup>3</sup>LC, tune green → red
- Emission for *ppy* emitters results primarily from a metal centered transition, <sup>3</sup>LC state for *ppy* λ<sub>max</sub> = 450 nm
- Blue shifted MLCT ⇒ more <sup>3</sup>LC character



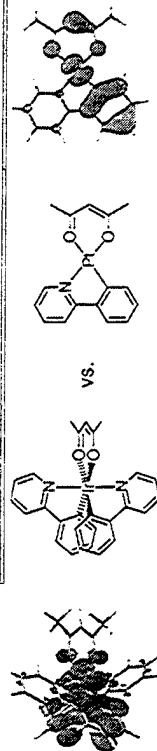
## Near 100% Efficiency



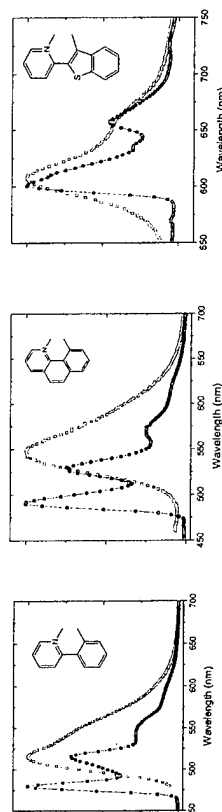
- Device structure: ITO/HTL/TAZ-(ppy)<sub>2</sub>Ir(acac)/BCP/Alq<sub>3</sub>/Li-Al
- Optimal doping concentration = 12%: high eff., low drive voltage
- η<sub>ext</sub> = (19 ± 1)%, η<sub>int</sub> = (87 ± 7)%, > 60 lum/W
  - η<sub>ext</sub> = 14% at 1000 Cd/m<sup>2</sup> (2 mA/cm<sup>2</sup>)

C. Adachi, *et al.*, *J. Appl. Phys.*, 2001

## LPt(acac) Compared to L<sub>2</sub>Ir(acac) Phosphors

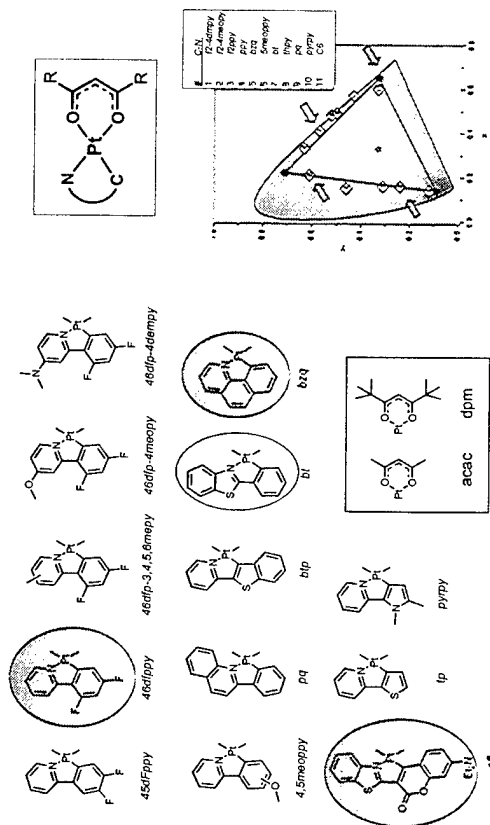


- MO pictures from DFT calculations, Spartan package
- Emission spectra LPt(acac) complexes are shown in blue and L<sub>2</sub>Ir(acac) complexes in red.
- All LPt(acac) complexes have lifetimes of 5-10 μsec, φ<sub>PL</sub> = 0.05-0.25 (solution, 298K).
- Complexes with MLCT excited state show significant blue shift, L = *ppy*, *bzq*.





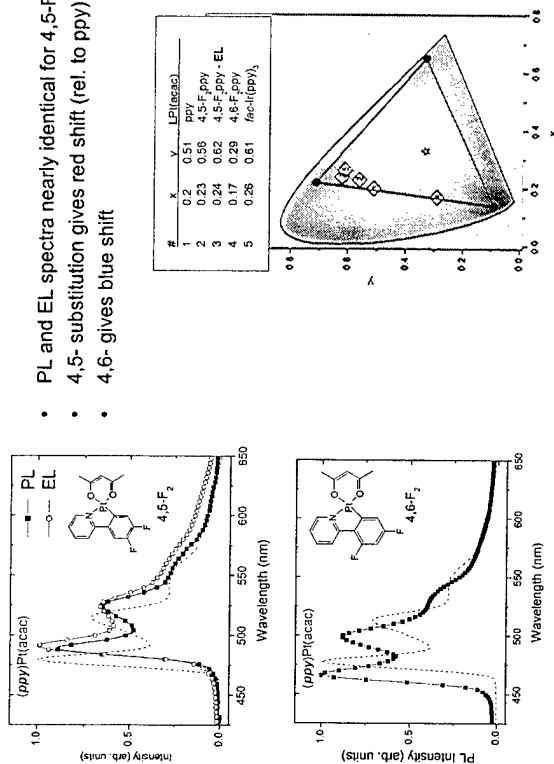
## Cyclometalated Platinum Complexes



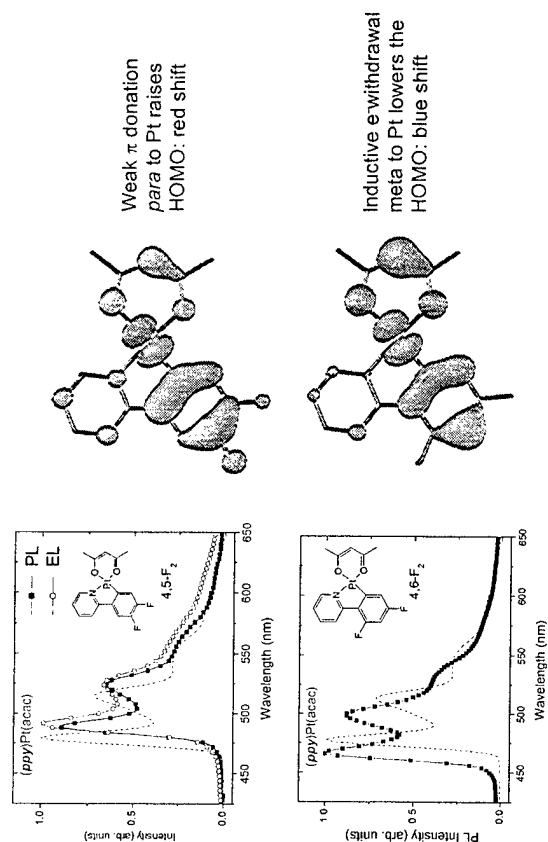
- Pt complexes have similar photophysics as the Ir analogs

## $F_2$ -ppyPt(acac) PL and EL

- PL and EL spectra nearly identical for 4,5- $F_2$ -ppy
- 4,5- substitution gives red shift (rel. to ppy)
- 4,6- gives blue shift



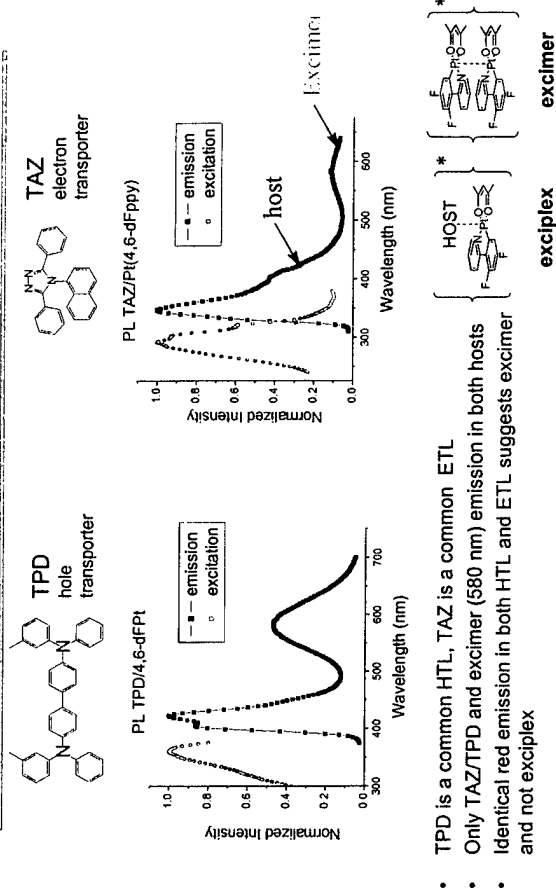
## $F_2$ -ppyPt(acac) PL and EL



Weak  $\pi$  donation  
para to Pt raises  
HOMO: red shift

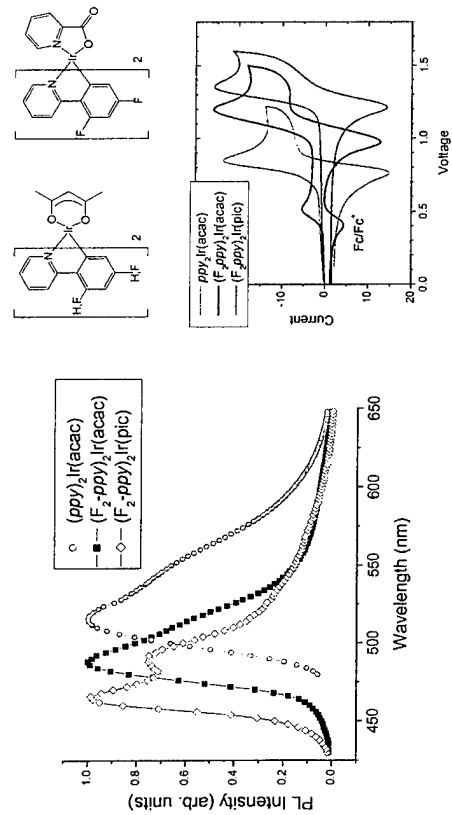
Inductive e-withdrawal  
meta to Pt lowers the  
HOMO: blue shift

## PL of Pt(4,6-dFppy)(acac) in OLED host materials



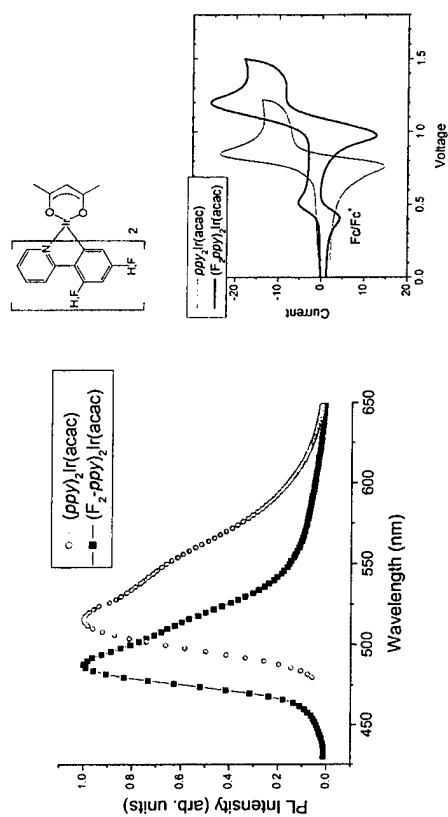
- TPD is a common HTL, TAZ is a common ETL
- Only TAZ/TPD and excimer (580 nm) emission in both hosts
- Identical red emission in both HTL and ETL suggests excimer and not exciplex

## (4,6-F<sub>2</sub>-ppy)<sub>2</sub>Ir(LX) solution PL/electrochemistry



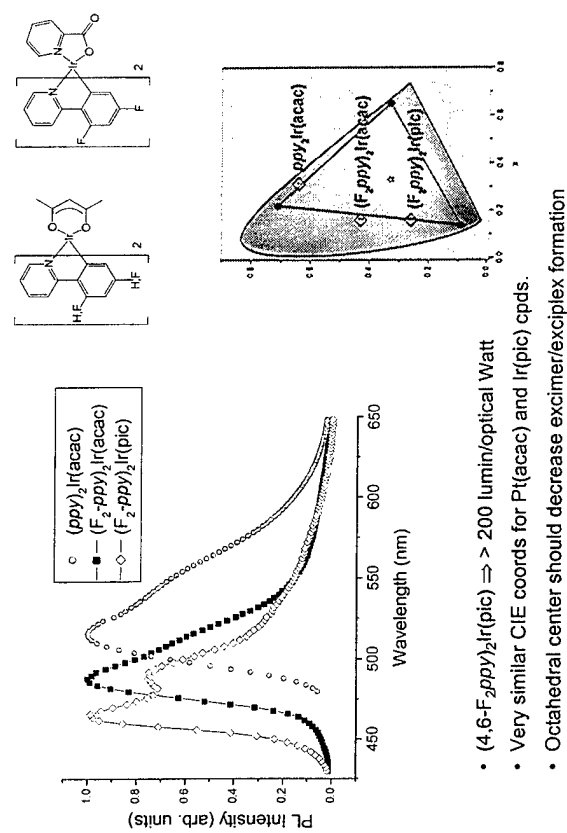
- pic substitution leads to further lowering HOMO, and blue shift in emission
  - 475 mV shift in the oxidation potential
  - 275 mV blue shift in emission
- Emission spectrum consistent with MLCT + <sup>3</sup>π-π\*

## (4,6-F<sub>2</sub>-ppy)<sub>2</sub>Ir(acac) solution PL/electrochemistry



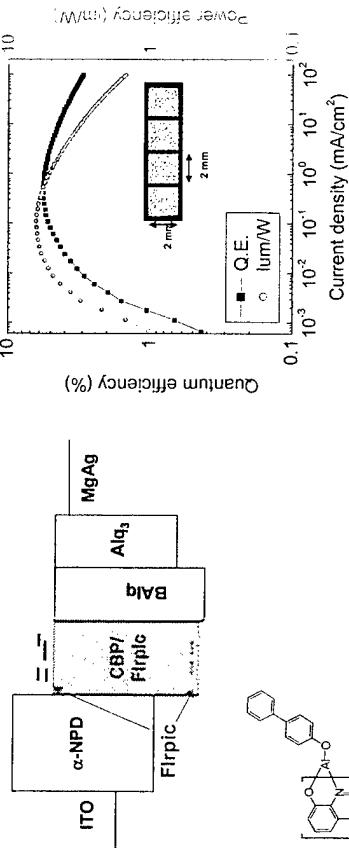
- Octahedral center ⇒ decrease exciplex formation
- F substitution leads to lowering HOMO, and blue shift in emission (MLCT)
  - 275 mV shift in the oxidation potential
  - 140 mV blue shift in emission

## (4,6-F<sub>2</sub>-ppy)<sub>2</sub>Ir(LX) solution PL/electrochemistry



- (4,6-F<sub>2</sub>-ppy)<sub>2</sub>Ir(pic) ⇒ > 200 lumin/optical Watt
- Very similar CIE coords for Ir(acac) and Ir(pic) cpds.
- Octahedral center should decrease excimer/excimer formation

## Blue Electrophosphorescence from Flrpic/CBP

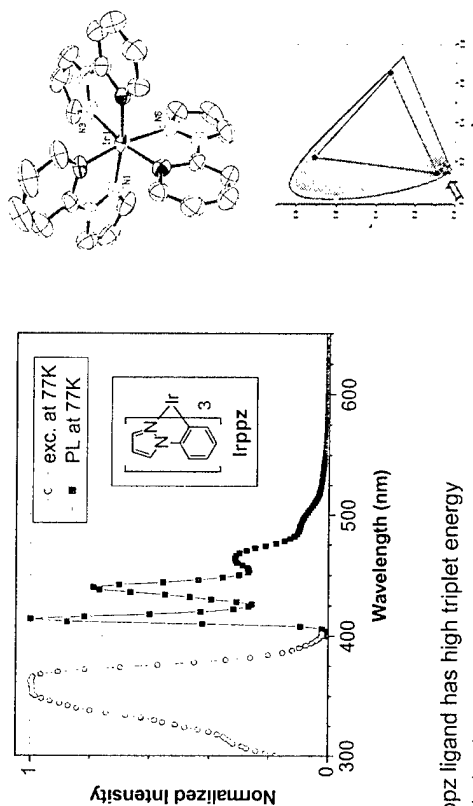


- Emission due solely to phosphorescent dopant
  - No excimer or exciplex
- Flrpic carries electrons in CBP
- Efficiency = 5.5%, > 5 lum/W, 12 cd/A at 100 cd/m<sup>2</sup>

C. Adachi, *et al.*, *Appl. Phys. Lett.* (2001)

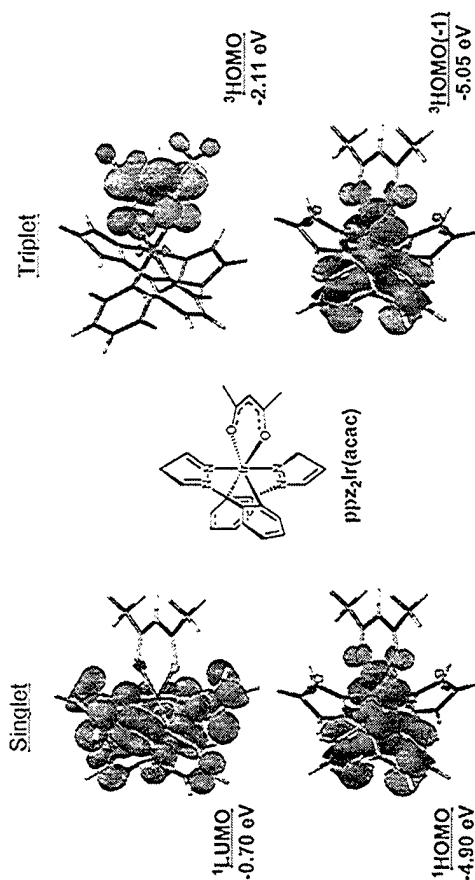
89

## Tris(1-phenylpyrazole) Iridium Complexes



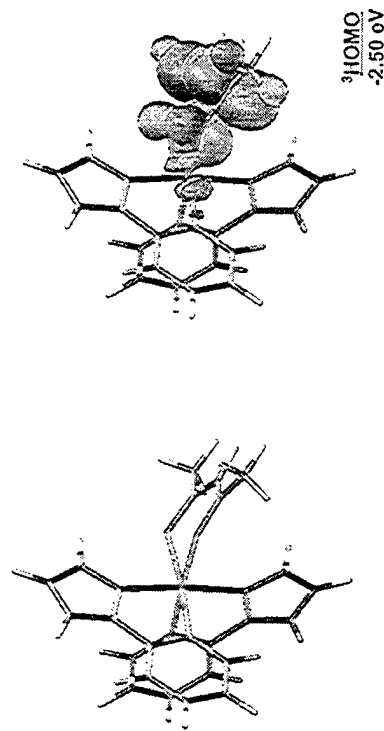
- ppz ligand has high triplet energy
- No luminescence at room temperature
- Are ppzlr derivatives inherently weak emitters?

## ppz<sub>2</sub>Ir(acac) Valence MOs



- Triplet is a charge separated state

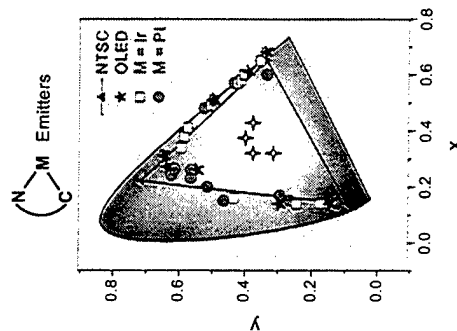
## Minimized Triplet Geometry for ppz<sub>2</sub>Ir(acac)



- Estimated triplet energy gap:
  - $\Delta E(\text{singlet-triplet}) \approx 2.40 \text{ eV}$  (517 nm, expt.)
- Significant geometry changes in the excited state  $\Rightarrow$  quenching
- LX ligands with higher triplet energies are needed to prevent quenching

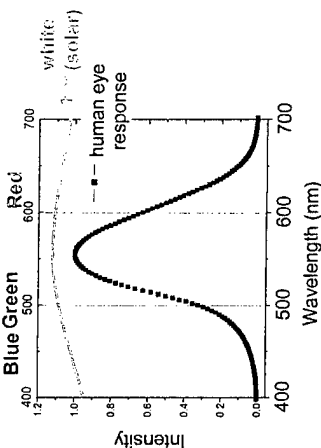
## Summary

- Careful control of the formation, confinement and relaxation of excitons can lead to highly efficient OLEDs
  - Metals are good, expensive metals are better
  - Both carrier and exciton trapping at the phosphor are critical for high efficiency
  - Using Ir based phosphors we have demonstrated  $\eta_{int} > 90\%$  for green,  $> 60\%$  for red, yellow and orange and  $> 25\%$  for blue
  - Lifetimes for green, orange and red devices  $> 50,000$  hours
- Careful design of ligands in Ir and Pt complexes leads to efficient, highly tunable phosphors for OLEDs
  - Control of the excited state
  - High efficiency regardless of color (blue, green, yellow, red)
  - Blue  $\rightarrow$  Red and White



## Color Mixing to Achieve White Emission

- You need a broad spectrum for good white illumination
- Color mixing with different colored OLEDs
  - Side-by-side arrangement of RGB elements, similar to flat panel display
    - Short R, G and B pixels together
  - Transparent devices can be stacked
    - Pixels on top of pixels with a common substrate
    - Large sheets of transparent R, G and B OLEDs can be stacked to achieve white



- Different dyes can be doped into emissive layer(s) of the OLED
  - multiple dopants in a single layer lead to complications due to energy transfer
  - segregate dopants into separate layers
  - How many emitters are needed?

## Acknowledgements

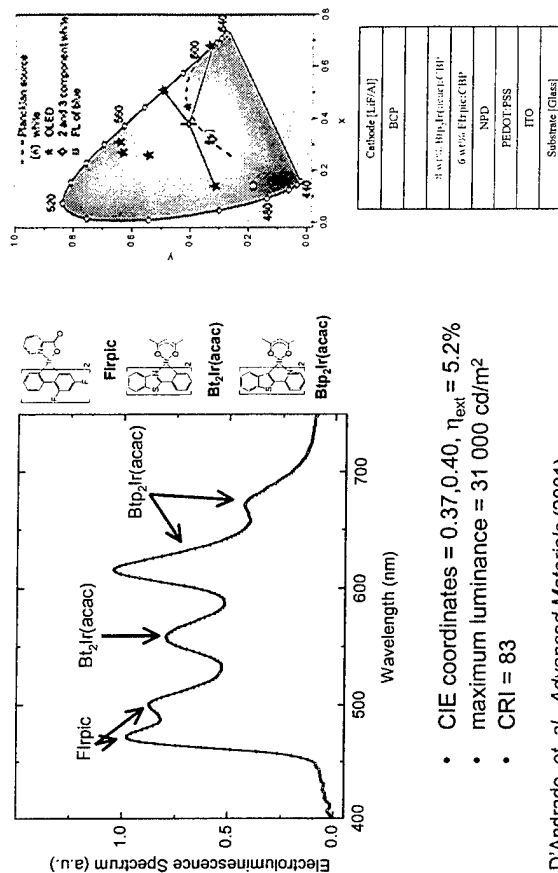
Jason Brooks, Vadim Adamovich, Peter Djurovich, Arnold Tamayo, Jian Li, Drew Murphy, Liza Babayan, Sergey Lamansky, Douglas Loy, Yujian You  
Chemistry, University of Southern California

Stephen Forrest, Brian D'Andrade, Marc Baldo, Paul Burrows  
Diarmid O'Brien Chihaya Adachi  
Electrical Engineering, Princeton University

Raymond Kwong, Mike Weaver, Julie Brown  
Universal Display Corporation

\$\$ Funding: Universal Display Corporation, NSF, DARPA

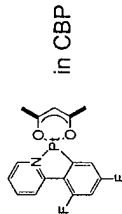
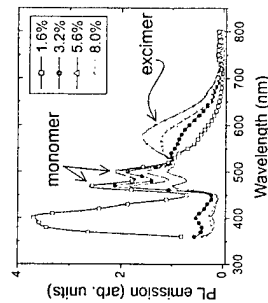
## Three phosphor white OLEDs: Each phosphor in a separate layer



- CIE coordinates = 0.37, 0.40,  $\eta_{ext} = 5.2\%$
- maximum luminance = 31 000 cd/m<sup>2</sup>
- CRI = 83

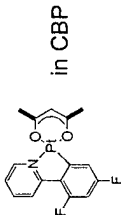
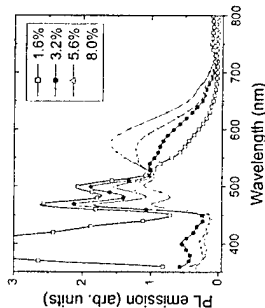
B. D'Andrade, et. al., Advanced Materials (2001)

## Single Dopant Monomer – Excimer Photoluminescence

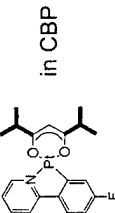
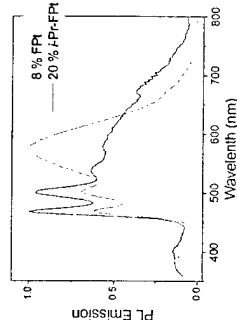


- monomer dopant emission at low doping level
- balanced monomer/excimer ca 5%
- CBP fluorescence at low doping levels
- increasing steric bulk can hinder excimer formation
  - could it lead to greater monomer/excimer ratio?

## Single Dopant Monomer – Excimer Photoluminescence

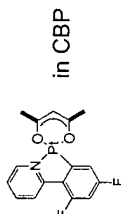
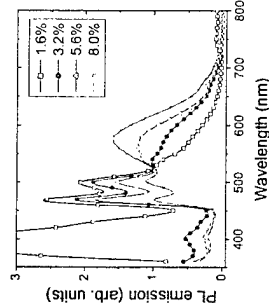


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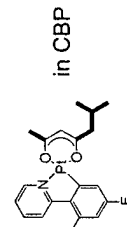
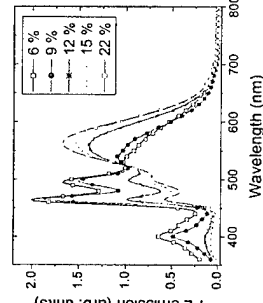


- replacing the methyl groups of FPI with *i*-Pr adds significant steric bulk
- Only weak excimer emission is observed at doping levels as high as 20%
- too much steric bulk gives only monomer, we need intermediate steric bulk

## Single Dopant Monomer – Excimer Photoluminescence

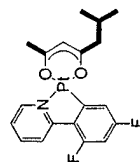


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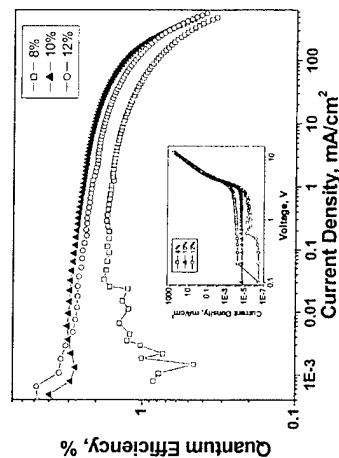
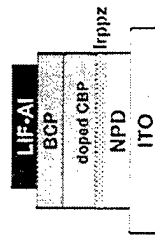


- Now FPI has one methyl and one butyl
- Excimer emission is now observed, and balanced monomer/excimer is seen between 9 and 12%, an ideal doping level for OLEDs

## High Efficiency Single Dopant WOLEDs

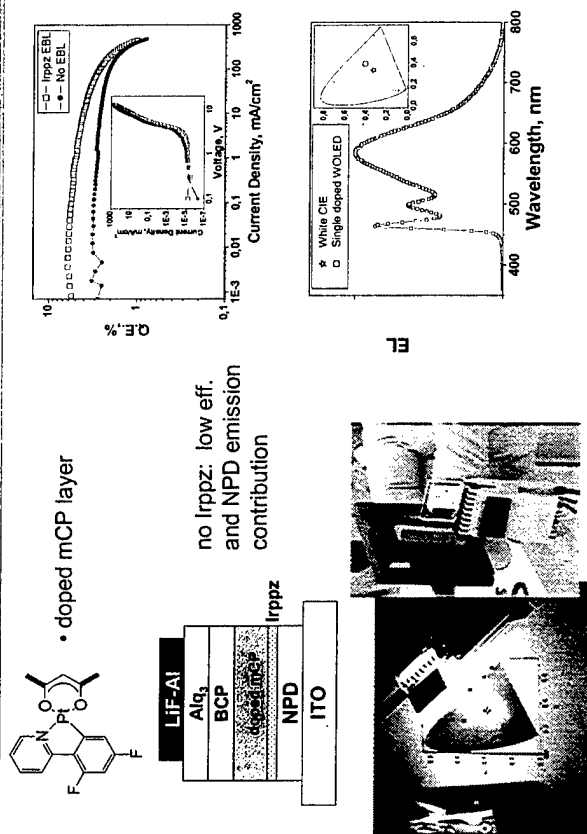


- doped luminescent layer
- only 4 organic layers and one dopant



Transfer is still endothermic

## High Efficiency Single Dopant WOLEDs



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## Cyclic Voltammetry and Ultraviolet Photoemission Data



The electron-rich phenylpyrazole ligand stabilizes the Co(IV) species produced electrochemically.

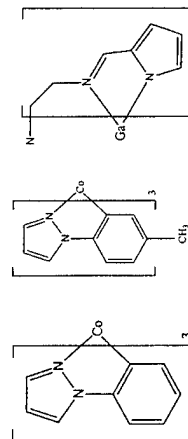
### UPS Data (HOMO)

CoPPZ: 5.37eV

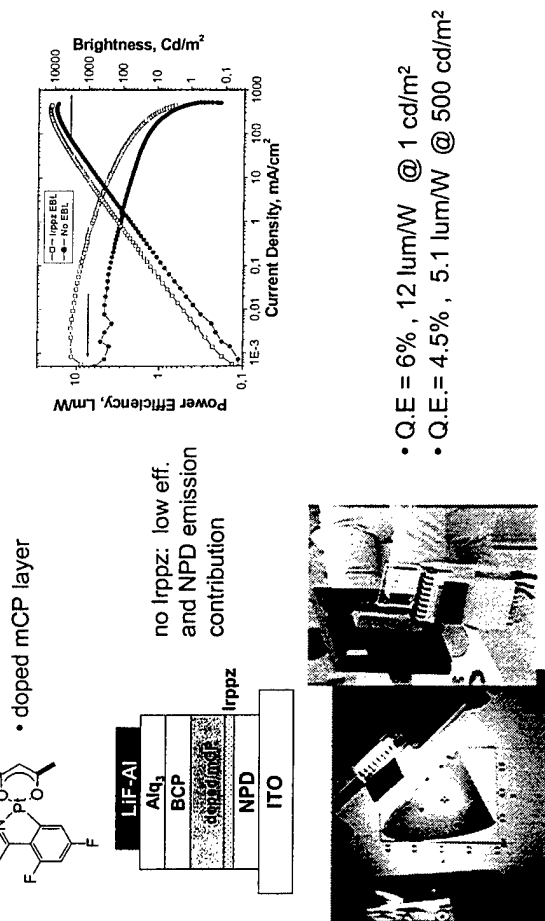
Co(mPPZ): 5.38eV

NPD: 5.51eV

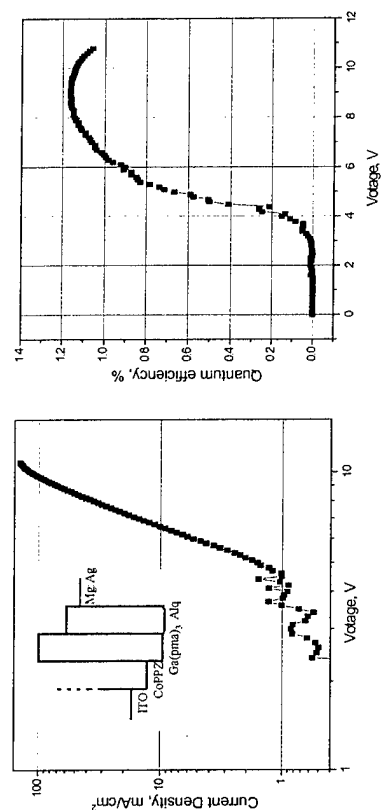
Gapma: 5.74eV



## Efficient OLED with ONLY Metal Complexes(I)



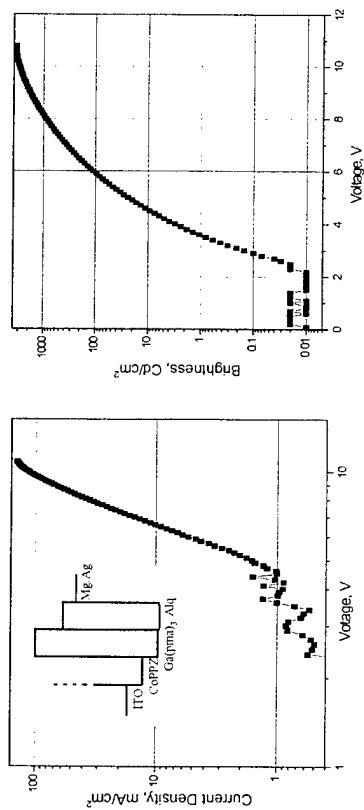
ITO/Coppz(400Å)/GaPMAEA(100Å)/Alq(500Å)/Mg:Ag(1000Å)/Ag(400Å)



Unfortunately, the device lifetime is poor with a Coppz HTL.

# Efficient OLED with ONI, V Metal Complexes(1)

ITO/Coppz(400Å)/GaPMAEA(100Å)/Alq(500Å)/Mg:Ag(1000Å)/Ag(400Å)



# DARPA HDS Final Program

## Review

5-3-02

Julie Brown

[jjbrown@universaldisplay.com](mailto:jjbrown@universaldisplay.com)

Universal Display Corporation

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# HDS UDC Program Objectives

- Demonstrate Reliability
- Fabricate Engineering Prototypes
- Design Pilot Line Facility

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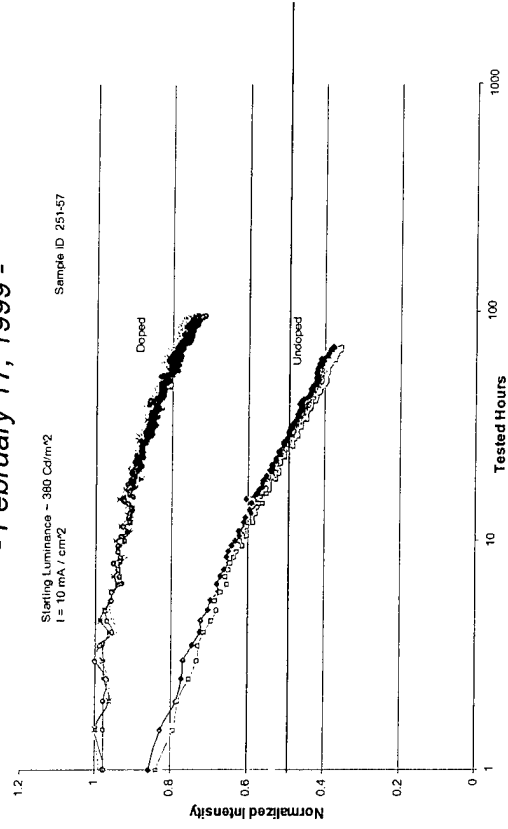
## Program Elements

- Reliability Task
  - » Life Test System
  - » Process and Packaging
  - » Phosphorescent OLEDs
- Display Prototype Task
  - » Passive Matrix Design
  - » TOLED Passive Matrix Prototype
  - » FOLED Passive Matrix Prototype
  - » Active Matrix Display Prototype
- Pilot Line Facility

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## OLED Lifetime: Doped vs Undoped

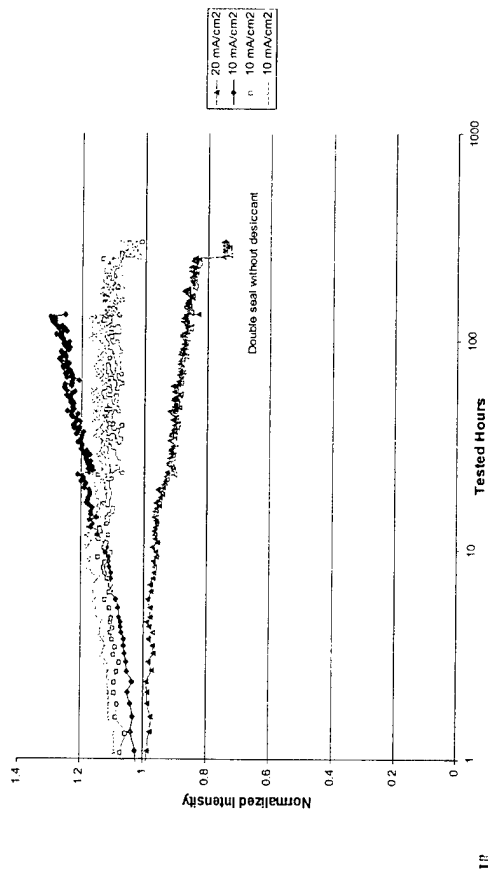
- February 17, 1999 -





# Red PHOLED Preliminary Data

- February 17, 1999 -



UNIVERSAL DISPLAY CORPORATION

## Red Phosphorescent OLED Lifetime

- April 19, 2000 -

### • Device Design

#### Sample A:

ITO(1500Å)/CuPc(200Å)/NPD(400Å)/CBP:PtOEP(300Å)/

Alq<sub>3</sub>(200Å)/Mg:Ag

#### Sample B:

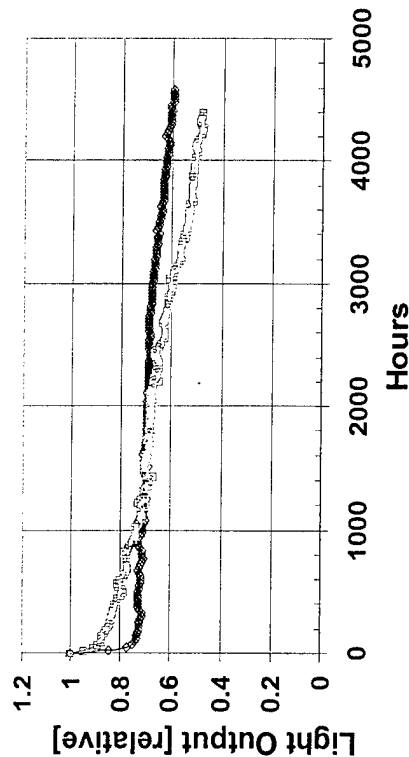
ITO(1500Å)/CuPc(200Å)/NPD(400Å)/Alq<sub>3</sub>:PtOEP(300Å)/

Alq<sub>3</sub>(200Å)/Mg:Ag

### Study of Lifetime Dependence on Phosphor Host

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## Red PHOLED Operational Stability



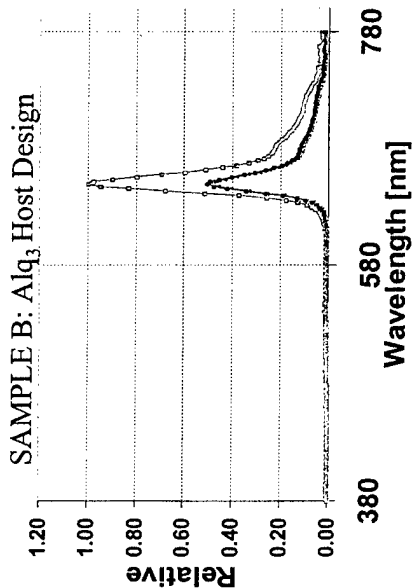
Alq<sub>3</sub> Host: Lifetime (50%) = 4000 hours

CBP Host: Lifetime(50%) = 8000 hours

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## Red OLED Spectral Response Stability



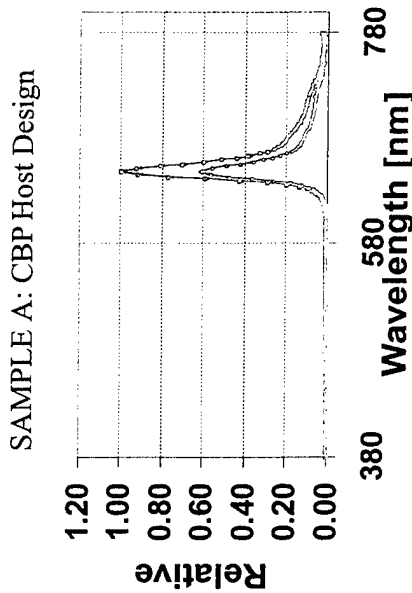
Comparison of response: t=0 and t=4500 hours

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April 19, 2000

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## Red PHOLED Spectral Response Stability



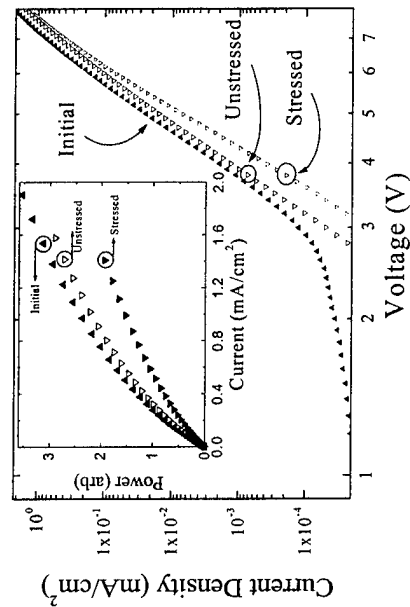
Comparison of response: t=0 and t=4500 hours

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## Red OLED LIV Stability

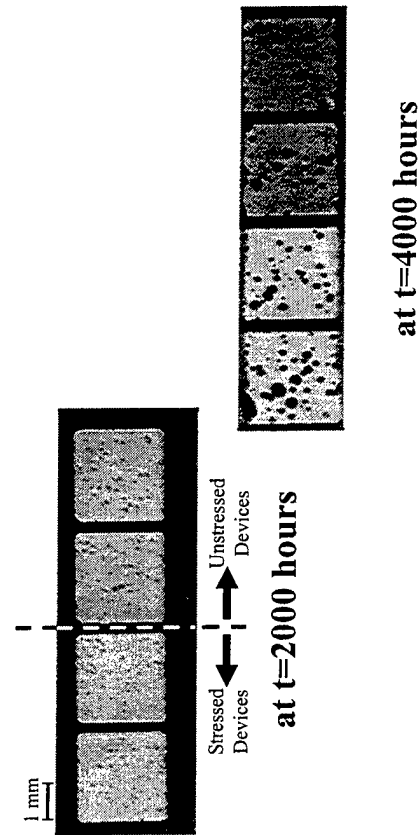
Sample A: CBP Host



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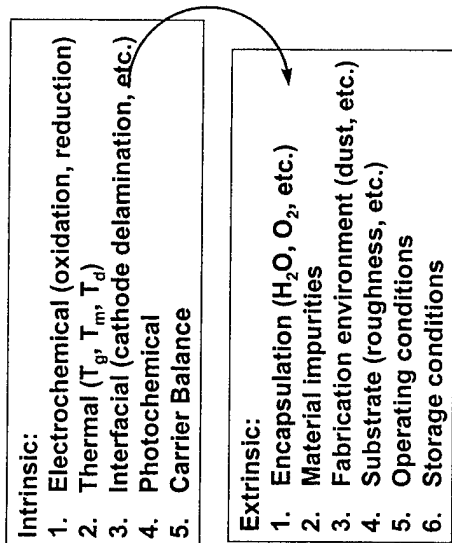
## Red PHOLED Package Failure



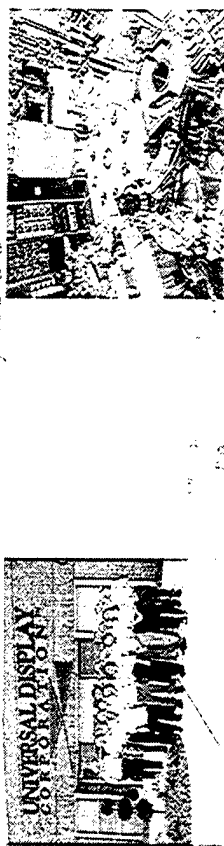
UNIVERSAL DISPLAY CORPORATION

April 19, 2000

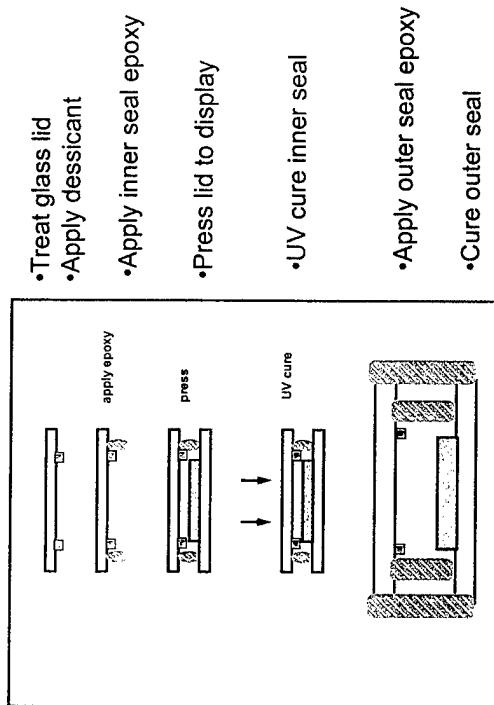
# Device Stability Interacting Factors



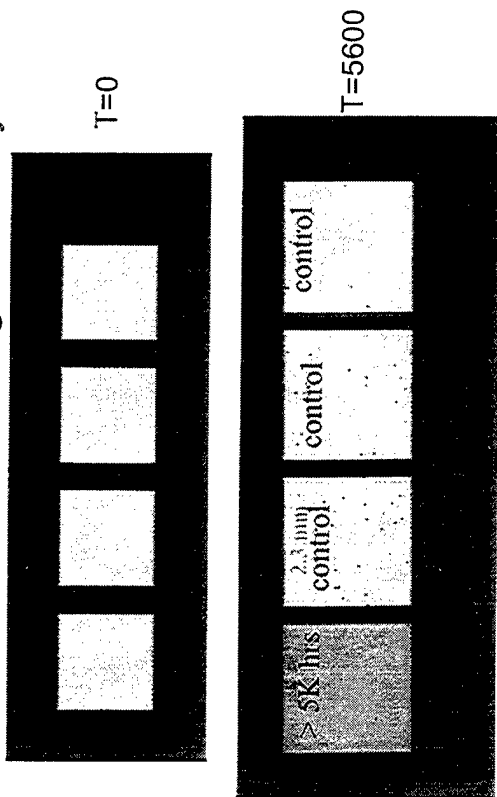
December 14, 1999



## Encapsulation Process Flow

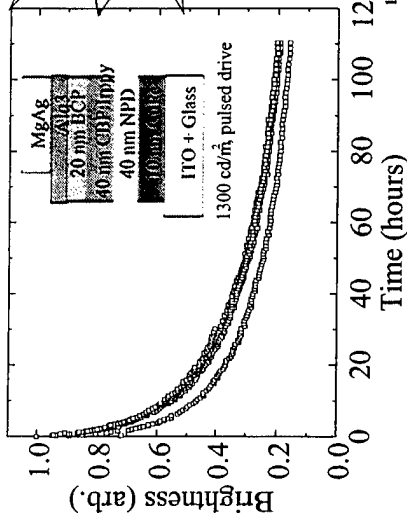


## Green PHOLED Package Stability

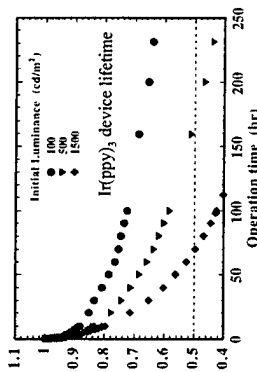


No pixel shrinkage observed after more than 5600 hours @ 500 nits

# Are Green Phosphors Stable?



Also, Tsutsui et al.  
*Jpn. J. Appl. Phys.* 38 in press...



BCP Crystallization?  
Phosphor Degradation?

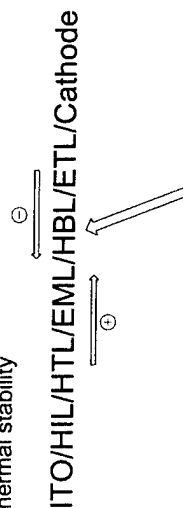
## Hole Blocking Materials

Basic requirements:

- Hole blocking (low HOMO level) and/or low hole mobility
- Electron transporting
- No quenching of the dopant emission

Stability issue:

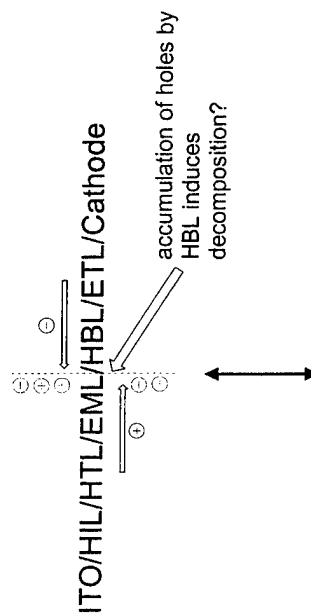
1. Anion stability
2. Thermal stability



what is the anion stability?  
what is the morphological stability?

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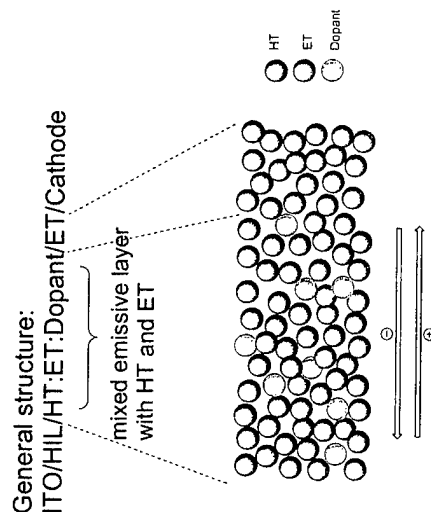
## OLED Design For Long Lifetime



What if the interface is absent?

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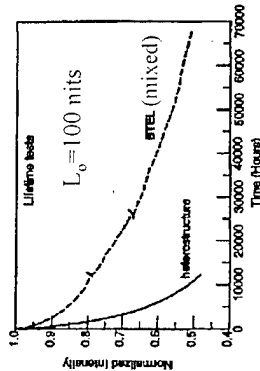
## Mixed Layer Devices



Largely reduced charge accumulation

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# Previous Mixed Layer Work



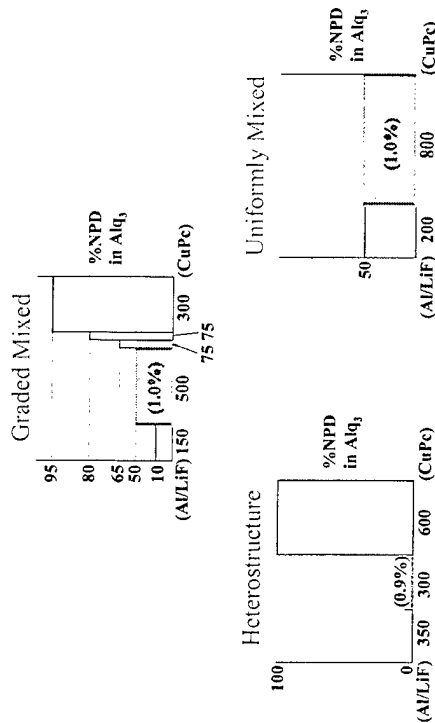
Choong et al., *APL* 75(2), 172 (1999)

Aziz et al., *Science* 283, 1900 (1999)

- Naka et al., *Jpn. J. Appl. Phys.* 33, L1772 (1994)
- Kido et al., *APL* 67, 2281 (1995)
- Wen et al., *APL* 71, 1302 (1997)

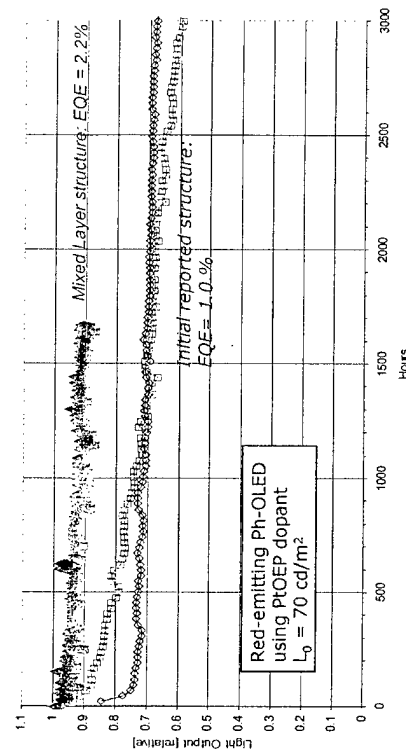
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# Device Structures- Current Study



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# Lifetime Comparison of Deep Red PHOLEDs



Mixed Layer PHOLED Lifetime Extrapolates to > 10<sup>6</sup> hours

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# Device Structures

Three basic device structures were employed in this study. The data presented correspond to the following structures, which contain a fluorescent green dopant (D):

■ Heterostructure	□ Graded Mixed	▲ Uniformly Mixed†
Al	Al	Al
LiF	LiF	LiF
Alq <sub>3</sub>	α-NPD:Alq <sub>3</sub> (90%)	α-NPD:Alq <sub>3</sub> (1:1)
Alq <sub>3</sub> :D (0.9%)	α-NPD:Alq <sub>3</sub> :D ((1:1):1.0%)	α-NPD:Alq <sub>3</sub> :D ((1:1):1.0%)
α-NPD	α-NPD:Alq <sub>3</sub> (35%)	CuPc
CuPc	α-NPD:Alq <sub>3</sub> (20%)	ITO
ITO	α-NPD:Alq <sub>3</sub> (5%)	
	CuPc	
	ITO	

\*NPD:Alq<sub>3</sub>=1:1 unless otherwise noted

†V.E. Choong et al., *APL* (1999), 75(2), 172

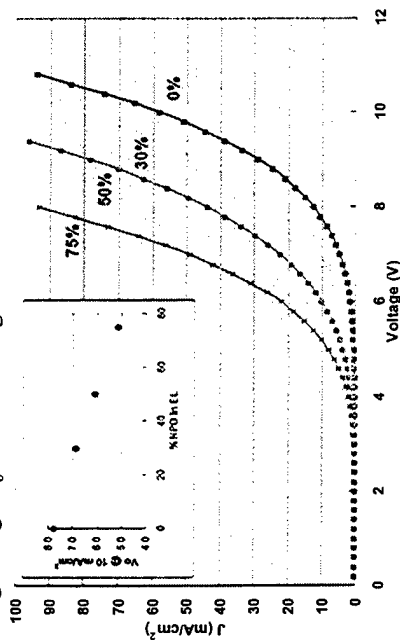
For comparative purposes, the properties of a device with a phosphorescent green dopant are also presented:

◆ PhosG : EML=CBP:Ir(ppy)<sub>3</sub>

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## J-V and $V_o$ Comparison

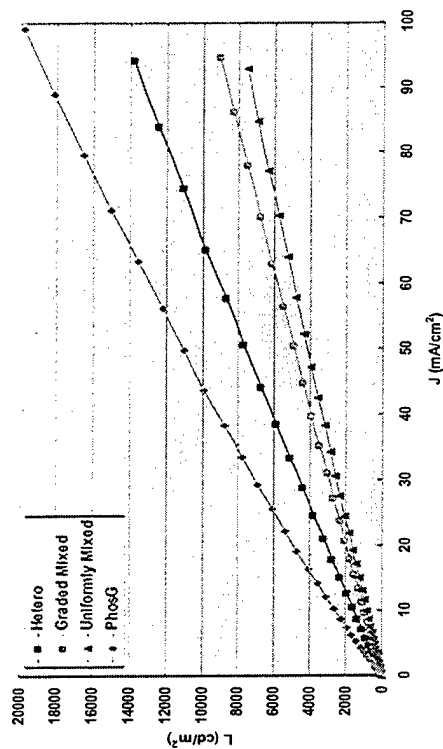
The dependence of the J-V characteristics on percentage of NPD in the emissive layer of the graded mixed devices is shown below (0% corresponds to the heterostructure). The inset illustrates the decrease in driving voltage  $V_o$  with increasing %NPD.



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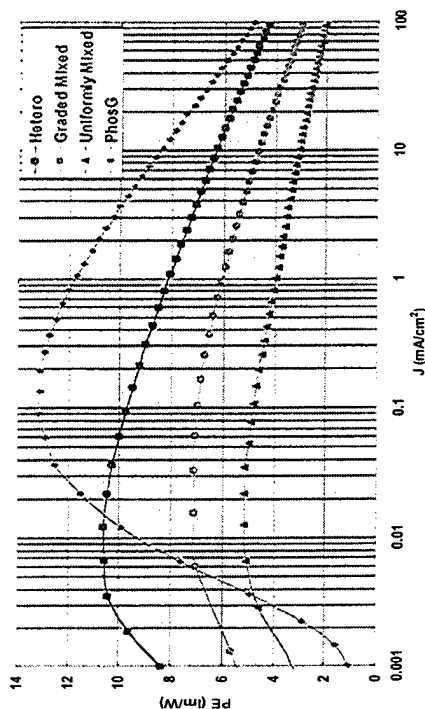
## Performance Comparison

Luminance vs. current density of the fluorescent and phosphorescent OLEDs:



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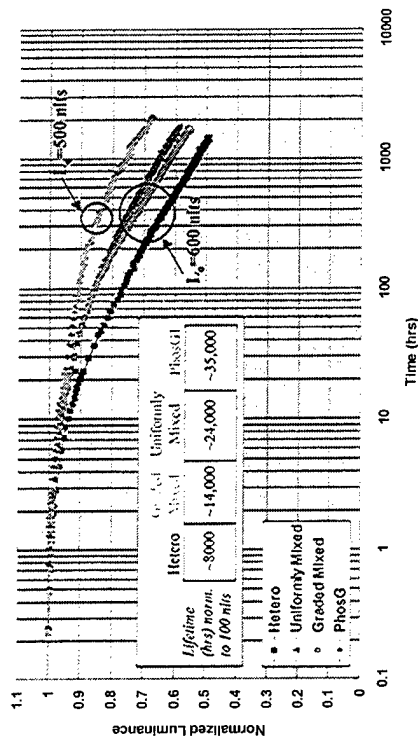
## Power Efficiency Comparison



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## Device Lifetime

The lifetime data (DC, constant current) show that mixing the HT and ET layers improves the lifetime of the device.



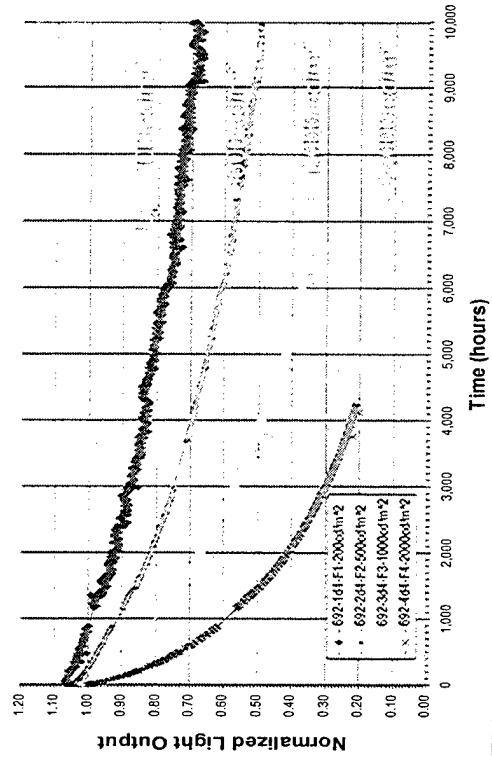
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# Data Summary

	Hetero	Graded Mixed	Uniformly Mixed	PhosG
Power Efficiency (lm/W) @ 100 nits	8.4	6.0	3.8	12.7
Driving Voltage (V) @ 100 nits	5.5	4.5	5.9	6.4
Lifetime (hrs) Normalized to L <sub>0</sub> = 100 nits (DC, const. J)	~8000	~14,000	~24,000	~35,000

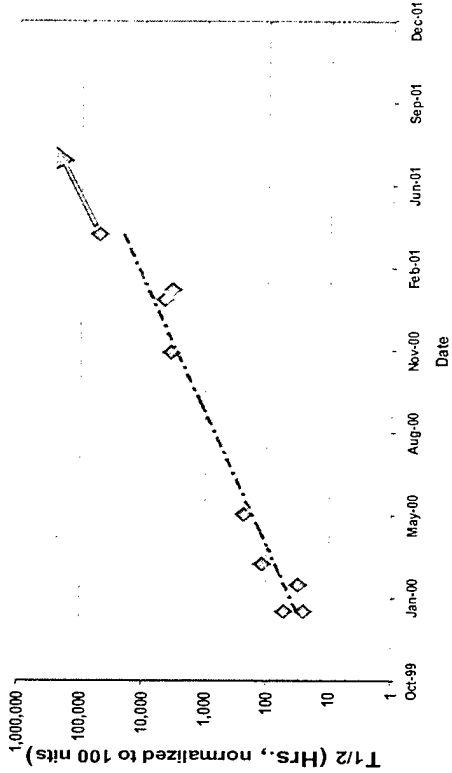
UNIVERSAL DISPLAY CORPORATION

# Green PHOLED Lifetime



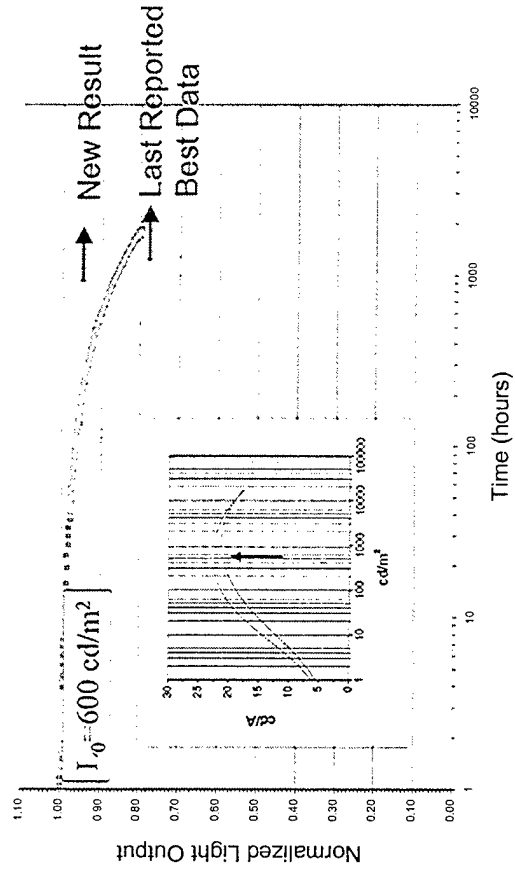
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# Green PHOLED Lifetime Progress



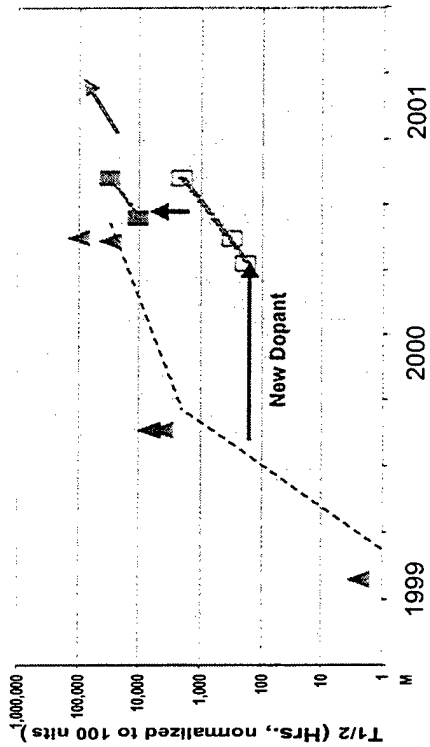
UNIVERSAL DISPLAY CORPORATION

# Green PHOLED New Results



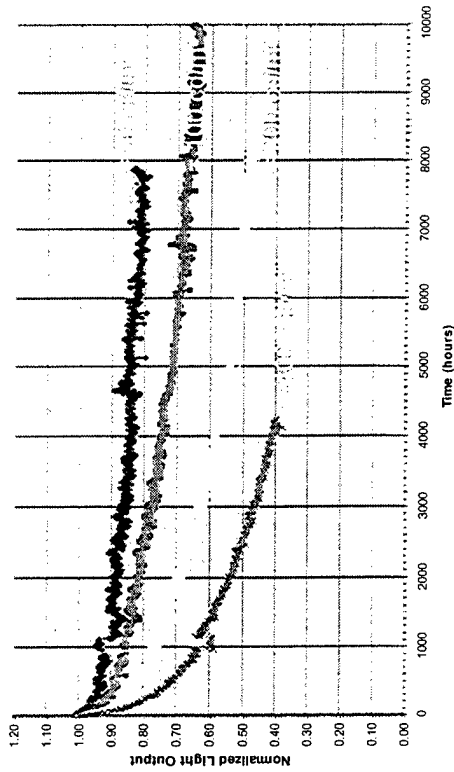
UNIVERSAL DISPLAY CORPORATION

# Red PHOLED Lifetime Progress



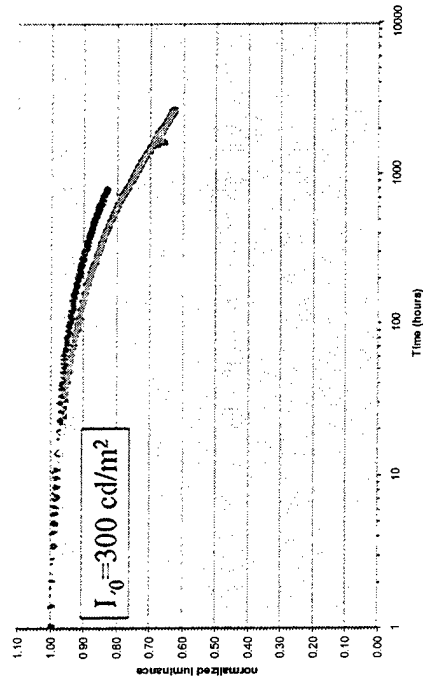
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# Mixed Layer Red PHOLED Lifetime



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# RED PHOLED Lifetime New Results

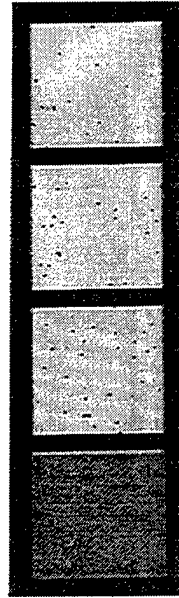
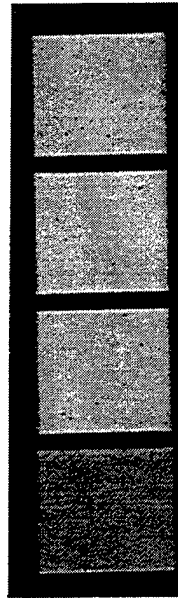


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# Red and Green PHOLEDs

$t = 10,000$  hours actual test time

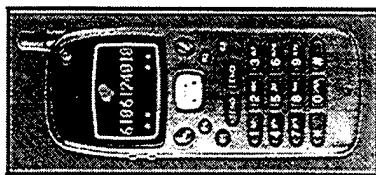
May 1, 2002



UNIVERSAL DISPLAY CORPORATION

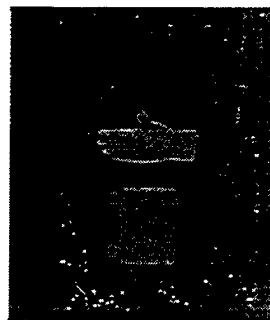
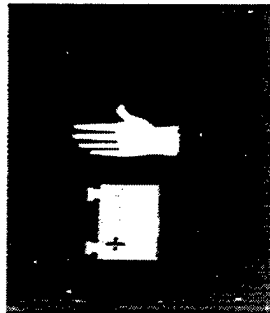


## Early Static OLED Prototype



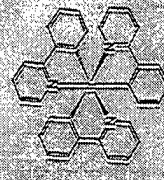
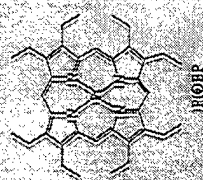
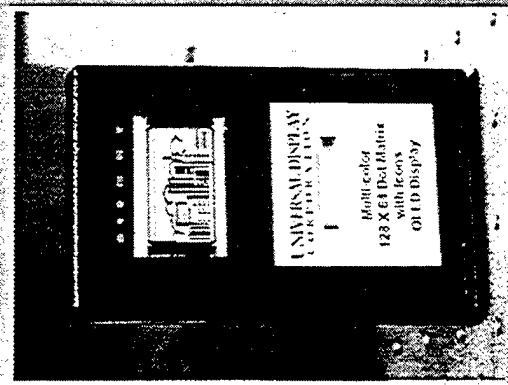
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CORPORATION

## Early SOLED Prototype



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CORPORATION

## First Passive Matrix Prototype



High efficiency materials

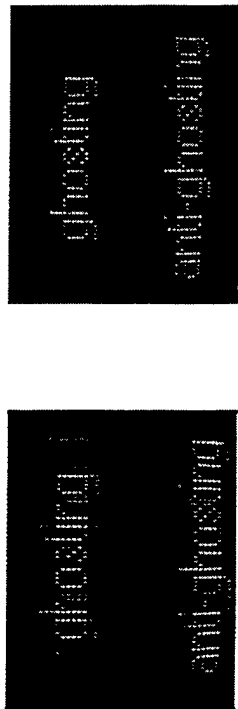
## Second Passive Matrix Prototype: PM2



- 128 columns x 64 rows, 80 dpi, 32-level gray scale
- peak current = 0.2 mA (1/64 duty cycle)
- driving voltage = 15V
- pixel active area = H 0.2275 mm x W 0.2475 mm = 0.0563 mm<sup>2</sup>
- pixel spacing = 0.3175 mm x 0.3175 mm
- fill factor = 56%
- average pixel luminance = 660 cd/m<sup>2</sup>
- at average pixel current density = 5.6 mA/cm<sup>2</sup>
- nonuniformity <10% (based on VESA FPD std)

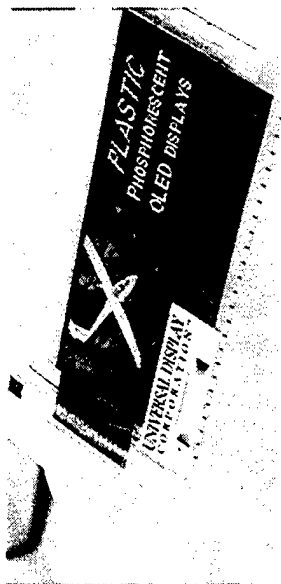
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Redesign of PM Drive Scheme: Eliminate Ghosting



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Third Passive Matrix Prototype: PM3



- 256 columns x 64 rows, 80 dpi, 256-level gray scale
- peak current = 0.19 mA (1/64 duty cycle)
- driving voltage = 16V typical,
- pixel active area = H 0.2275 mm x W 0.2275 mm = 0.0518 mm<sup>2</sup>
- pixel spacing = 0.3175 mm x 0.3175 mm
- fill factor = 51%
- average pixel luminance = 300 cd/m<sup>2</sup> (without circular polarizer)
- at average pixel current density = 2.9 mA/cm<sup>2</sup>
- nonuniformity <10% (based on VESA FPD std)

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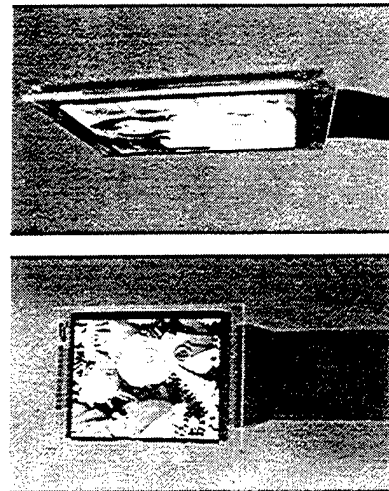
Digital Camera prototype with OLED display: PM4



- Configured to be digital camera or compact video monitor with freeze frame
- 240 columns x 64 rows, 80 dpi, 64-level pulse width modulation gray scale using off the shelf driver chips
- Peak pixel current = 0.18 mA (1/64 duty cycle)
- Driving voltage = 16V typical, maximum system voltage 18V
- Average pixel luminance = 150 cd/m<sup>2</sup> with circular polarizer
- at average pixel current density = 2.9 mA/cm<sup>2</sup>
- Four hours with fully charged batteries
- Compact size - 4.5" x 2.5" x 1.25"

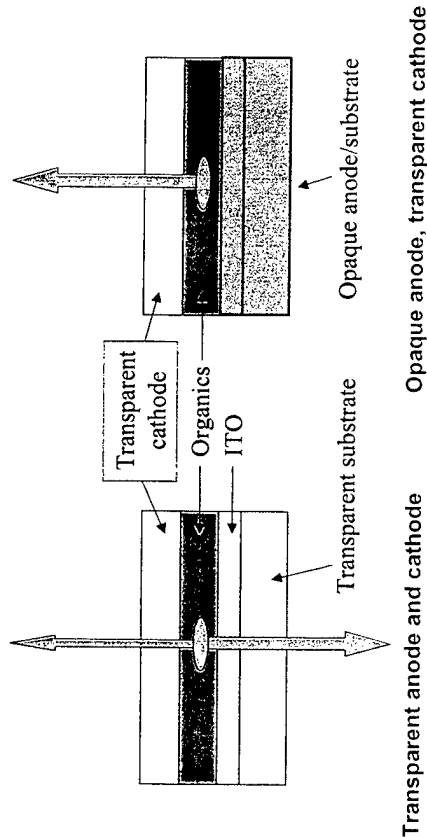
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Samsung SDI 2.2" Full-color Display UDC R/G PHOLEDs



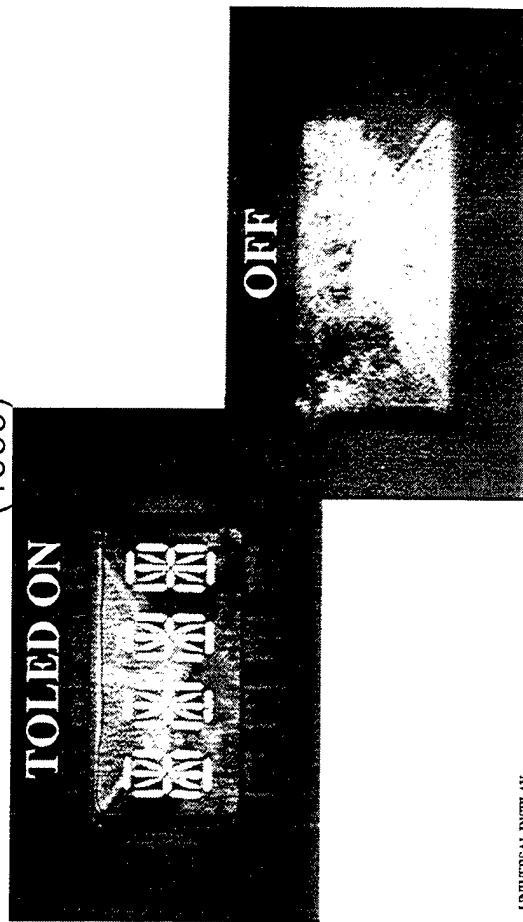
ITEMS	SPEC.
Diagonal size (in.)	2.2
Pixel Format	176 (H) x RGB x 220 (V)
Pixel pitch (µm)	66 x 198
Pixel density (in. <sup>-2</sup> )	128
Panel size (mm <sup>2</sup> )	41.976 (H) x 56.232(V)
Aperture ratio	32%
Luminance (w/o polarizer)(cd/m <sup>2</sup> )	200
White Quality	Peak : >300 (0.31,0.32)

## Transparent vs. Top Emission OLEDs



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## Transparent OLED (TOLED) 1<sup>st</sup> Prototype (1999)



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## Transparent OLEDs



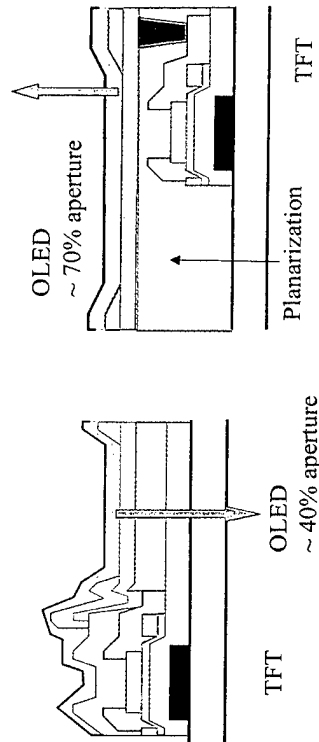
Future vision-area applications

- Top emission for active matrix displays
- Stacked RGB Emitters (tunable color)

Funding from DARPA via AFRL, and US Army (CECOM - NVESD)

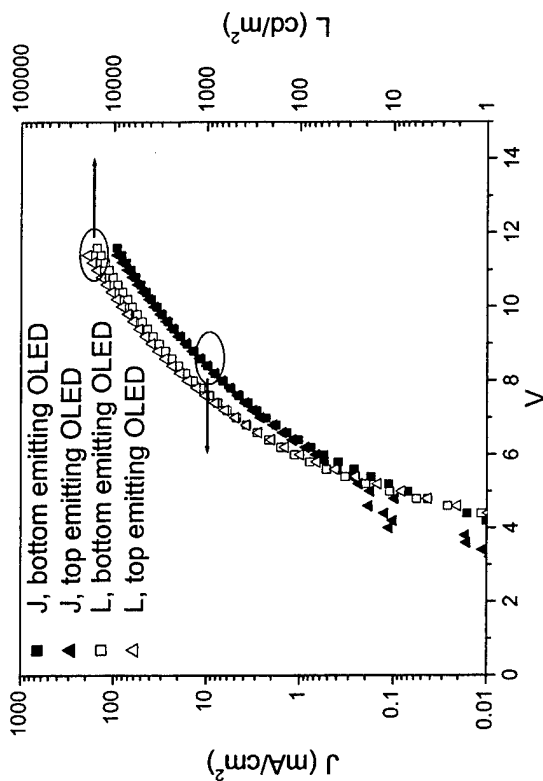
## Technical Merits of Top Emission OLEDs

- Potentially higher efficiency than bottom emission device. We have demonstrated TOLEDs as efficient as the bottom emission device on a reflective anode.
- Allows a higher aperture ratio in AMOLED pixels.



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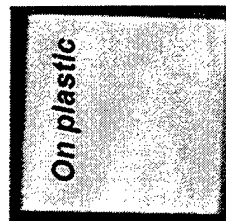
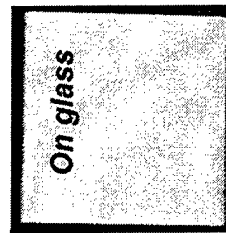
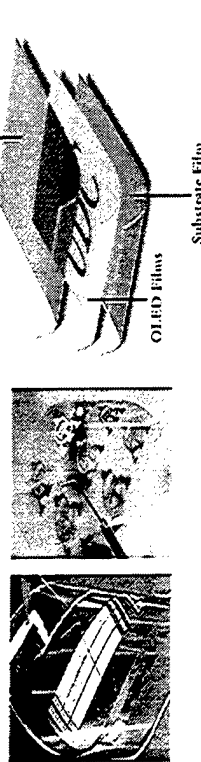
## Green Top Emission Devices



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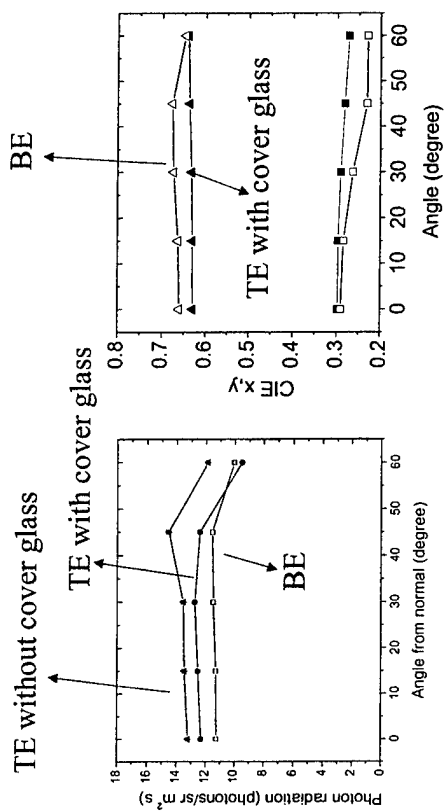
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## Flexible OLEDs (FOLEDs)



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## TOLEDs with and without a Cover Glass



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## Key FOLED Issues

### Packaging

- Permeability/OLED lifetime
- Conformability, flexibility
- Press durability

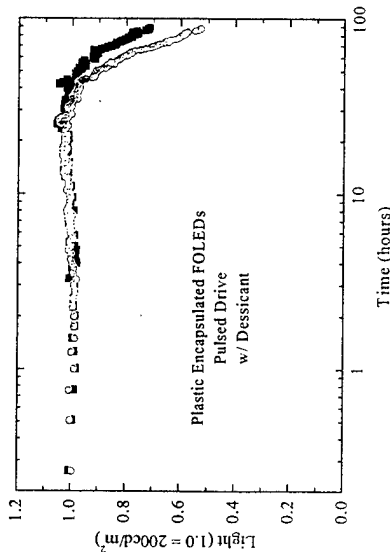
### Yield

- Substrate processability
  - Temperature and chemical resistance, surface roughness
  - ITO performance and patternability
- ### Display Fabrication
- Passive/active matrix architecture
  - Module assembly

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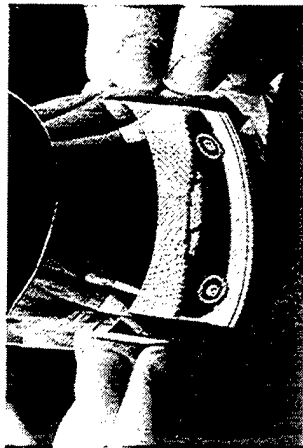
# Plastic Encapsulated FOLED

Plastic with No Barrier Coating



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# Flexible Display Prototypes



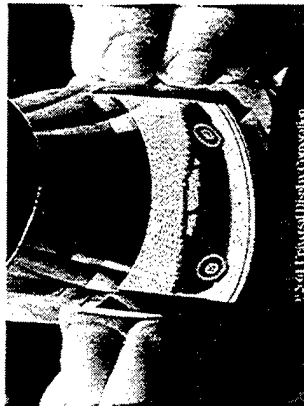
Passive Matrix Built on ITO/Plastic



Passive Matrix Built on Battelle Barrier Coated Plastic

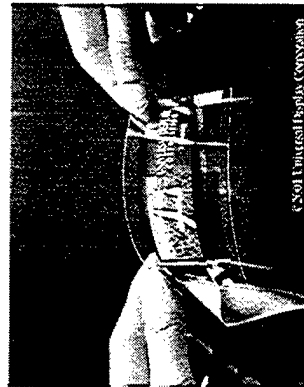
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# Flexible Display Progress



2000

- 64 x 128 passive matrix display
- 60 dpi resolution
- 60 Hz refresh rate
- 0.175 mm PET substrate



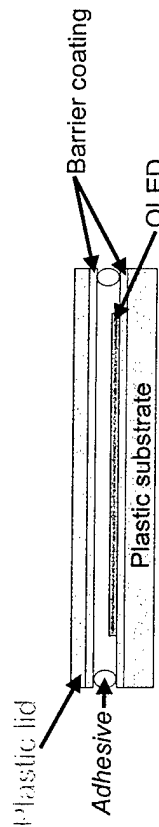
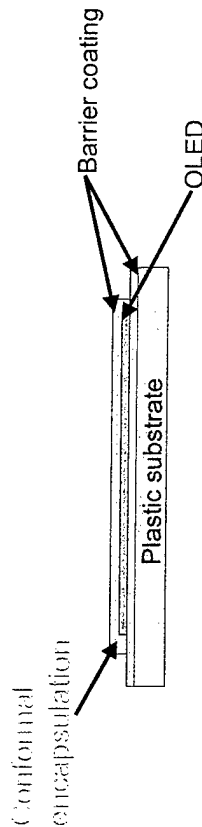
2001

- 64 x 240 passive matrix display
- 80 dpi resolution
- 120 Hz refresh rate
- 0.175 mm PET substrate
- full motion video

U.S. Patent No. 5,844,363

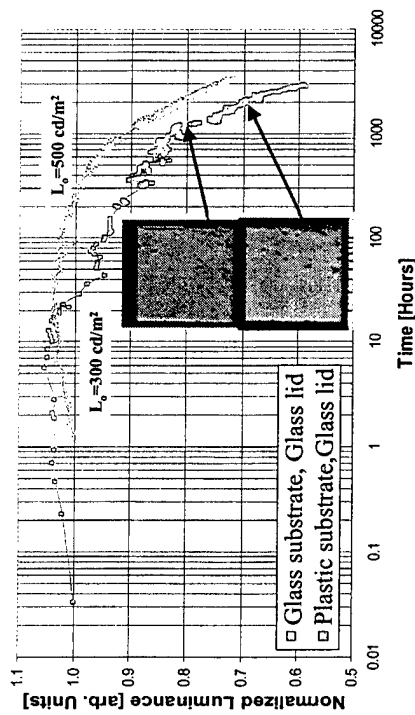
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# Flexible Packaging Options



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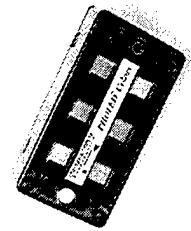
# Lifetime of OLEDs on Plastic vs. Glass



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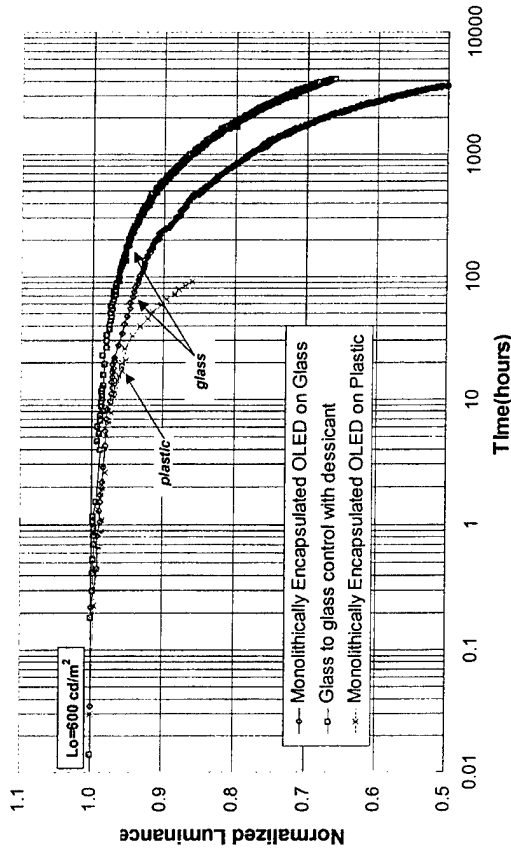
## Phosphorescent OLED Performance

EL color	Deep red	Red	Blue	Green
Peak wavelength (nm)	650	620	474	514
CIE - x	0.71	0.65	0.16	0.30
CIE - y	0.29	0.35	0.37	0.63
Luminance eff @ 1 mA/cm² (cd/A)	1.0	11	13	24
Lifetime (hours)	100,000 @ 70 cd/m²	>7,000 @ 300 cd/m²	under development	>8,000 @ 500 cd/m²



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# Evaluation of Monolithic Encapsulation



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## Other Key Accomplishments Since 1997

- Transparent/Top Emission TOLEDs
  - Efficiency as high as Bottom Emission
  - Lifetime > 3,000 hours
- Flexible OLEDs
  - Process Yield Understood
  - Demonstrated World's First FOLED Display
  - On our way to enhancing lifetime

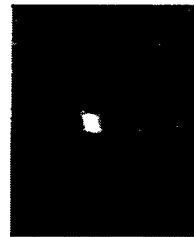
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## What directions are we headed?

- in the areas from the HDS legacy -
- Reliability
  - Developing Epoxyless Packages
  - Developing New Materials and Improved Architectures
  - Maximizing the Efficiency x Lifetime Product
  - Investigating High Temperature Operation
- Prototypes
  - Flexible Displays
  - AMOLED Prototypes with Partners
  - Transparent Displays
- Pilot Line.... I.e. building the business

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## First OLED on OVPD Pilot Line System

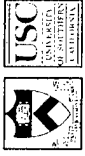


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## The Business

### TECHNOLOGY DEVELOPMENT

- Cutting-edge research & development
- Expanding intellectual property portfolio
- Process development & product prototyping



### TECHNOLOGY TRANSFER

- Patents, know-how and training
- High-purity organic materials
- Next-generation OLED deposition equipment



### COMMERCIALIZATION PARTNERSHIPS

- Co-development programs
- Licensing
- Joint ventures



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